Contaminated Soil '98

Proceedings of the Sixth International FZK/TNO Conference on Contaminated Soil, 17–21 May 1998, Edinburgh, UK

Volume 2

Thomas Telford

Published for the organizers by Thomas Telford Publishing, Thomas Telford Ltd, 1 Heron Quay, London E14 4JD. URL: http://www.t-telford.co.uk

Distributors for Thomas Telford books are
USA: ASCE Press, 1801 Alexander Bell Drive, Reston, VA 20191-4400, USA.
Japan: Maruzen Co. Ltd, Book Department, 3–10 Nihonbashi 2-chome, Chuo-ku, Tokyo 103
Australia: DA Books and Journals, 648 Whitehorse Road, Mitcham 3132, Victoria

First published 1998

A catalogue record for this book is available from the British Library

The paper used in this book is acid-free and totally chlorine-free. The pulp came from sustainable, managed forests in which at least one tree is planted for every one felled.

ISBN: 0 7277 2675 7

© The authors, 1998, unless otherwise stated

All rights, including translation, reserved. Except for fair copying, no part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying or otherwise, without the prior written permission of the Books Publisher, Thomas Telford Publishing, Thomas Telford Ltd, 1 Heron Quay, London E14 4JD.

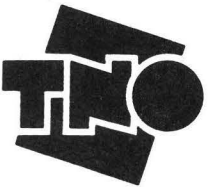
This book is published on the understanding that the author is/authors are solely responsible for the statements made and opinions expressed in it and that its publication does not necessarily imply that such statements and/or opinions are or reflect the views or opinions of the publishers or of the organizers.

Printed and bound in Great Britain by Redwood Books, Trowbridge, Wiltshire

ConSoil '98
Sixth international FZK/TNO conference on contaminated soil

The conference was organized by the Research Centre Karlsruhe (FZK, D), and The Netherlands Organization for Applied Scientific Research (TNO, NL), in cooperation with Scottish Enterprise (UK). It was supported by governments and agencies from these and other countries.

Forschungszentrum Karlsruhe
Technik und Umwelt



Scottish Enterprise

Contents overview

Volume 1

Contents

Scientific committee, scientific advisory board, organizing committee, secretariat and supporting organizations

Foreword

Opening session

Lecture and workshop sessions

Theme A: International cooperation

Theme B: Policies and strategies, governmental and industrial standards and protocols

Theme C: Investigation and characterization, behaviour and fate of contaminants and analyses

Theme D: Risk assessment, quality and health criteria

Theme E: Remediation and treatment technologies, research and development and proven technologies

Theme F: Land reuse, legal and financial development, management of contaminated land

Index of keywords

Index of authors

Volume 2

Contents

Short communications

Theme A: International cooperation

Theme B: Policies and strategies: governmental and industrial standards and protocols

Theme C: Investigation and characterization, behaviour and fate of contaminants and analyses

Theme D: Risk assessment, quality and health criteria

Theme E: Remediation and treatment technologies; research and development and proven technologies

Theme F: Land reuse, legal and financial development, management of contaminated land

Country sessions

Technical tour

Index of keywords

Index of authors

Contents

Short communications

Theme A: International

Experimental and theoretical study of the effect of pressure on thermal decontamination of soils polluted by hydrocarbons
Risoul V., Trouvé G., Gilot P. 719

The Scottish Contaminated Land Forum (SCLF): a collaborative approach to contaminated land assessment
Pollard S.J.T, Gould J., Flowers H. 721

Soil management in European ports
Ammerlaan R.A., Engelhardt D. 723

Knowledge transfer to Eastern Europe: learning by experience
Goldsborough D.G., Smit P.J. 725

RTDF bioremediation of chlorinated solvents consortium
Bell M.J., Ellis D.E, Gannon D.J., Klecka G.M., Licarta J., Meiers D.T., Major D.W., Salvo J.J., Sayles G.D., Vogel C.M., Woodworth R. 727

The Amsterdam questionnaire
Visser W., Elkenbracht E., Martin I., Johnson S., Bardos P. 729

The ad hoc international working group on contaminated land
Visser W.J.F., Skovgaard I.M., Hoppener C. 731

International networks on contaminated land – an overview
Kasamas H., Denner J., Skovgard I.-M., Bardos P. 733

Theme B: Policies and strategies: governmental and industrial standards and protocols

The French national approach to a simplified risk assessment
Darmendrail D., Sauvalle B. 743

Release of the Netherlands guideline on soil protection at industrial sites (NRB)
Ruardi P.A., van Sandick O.Z. 745

Implementation of Title IX of the European basic safety standards directive concerning interventions as a result of radioactive mining relics into German law
Wichtery K., Przyborowski S., Sangenstedt Ch. 749

Hazards and protective measures associated with the handling of biological agents during soil remediation
Schies U. 751

Criteria for selecting health risk levels to define soil clean-up objectives
Empereur-Bissonnet P., Dab W., Dor F. 753

An integrated regulatory approach for risk assessment and the development and use of guideline values for contaminated land remediation in the UK
Harris R.C., Herbert S. 755

A priority system for the ranking of contaminated sites
Bronders J., Cornelis C., Geuzens P., Nouwen J., Ceenaeme J. 757

Development of clean-up values for soil pollution in nature reserves
Goyvaerts M.P., Cornelis C. 759

Contaminated land in Scotland: the impact and challenge of the new statutory regime
Sutherland W. 761

Quality assurance for site investigation in the Netherlands
de Koning W., de Groof A.A. 763

The classification of contaminated material in highway earthworks
Wilson P., Perry J., Reid J.M. 765

Soil remediation in Flanders new policies and strategies
De Nijs W., Van Dyck E., Wille E., Ceenaeme J. 767

Safety and health protection in the remediation of contaminated sites
Feige-Munzig A.P. 769

Contaminated sites for the evaluation of potential technologies – *CONSEPT*
Bardos R.P., Johnson S., Laidler D. 771

Systematic investigation into 350 sites with suspected warfare-related environmental damage in Bavaria
Kaukal B., Schneider R., Schäfer J. 773

Risk communication for contaminated land: a framework for managing public concern
Kemp R., Valledy B., Quint M., Pollard S.J.T., Forster V., Crowther Y., Jeffries R., Aston S. 775

Environmental criminalistics at the Netherlands forensic science laboratory
Korthagen E.J., Vermeij E.J. 777

Japan's guidelines for surveys and measures for soil and groundwater pollution, and a new system to protect groundwater from contamination
Fukumorita T. 779

Site specific risk assessment for ecosystems
Rutgers M., Notenboom J. 781

Target values and background levels in the Netherlands: how to define good soil quality
Lamé F.P.J., Leenaers H. 783

The impact of micropollutants from non-point sources on soil quality in the Netherlands
Franken R.O.G. 785

Theme C: Investigation and characterization, behaviour and fate of contaminants and analyses

Physical/chemical treatment of contaminated soil to enhance the biological availability of hydrophobic compounds
Bonten L.T.C., Grotenhuis J.T.C., Rulkens W.H. 789

Degradation of polycyclic aromatic hydrocarbons (PAH): pollutant accessibility and efficiency of soil microflorae
Haeseler F., Blanchet D., Druelle V., Werner P., Vandecasteele J.P. 791

Contamination of aquifer A coused by lagoons with liquid waste
Belic A., Dalmacija B., Belic S. 793

The performance of diagnostic chemical indices for oil-contaminated sites
Whittaker M., Pollard S.J.T. 795

Bioavailability of PAHs in soil and ecotoxicological considerations
Loibner A.P., Szolar O., Schlegl M., Gartner M., Braun R. 797

***Site-ASSESS*, a decision support system for designing sampling strategies**
Ferguson C.C., Tucker P., Nathanail C.P. 801

How many samples? Balancing cost against risk in sampling design
Ferguson C.C. 803

Natural biological treatment of polluted sediments
Harmsen J. 805

Dielectric measurements of clay as a potential method of contaminant detection
Carrier M., Soga K. 807

Development of quality management plans for testing de-contamination technologies for soil and groundwater
Siebert J., Heuel-Fabianek B., Steffens K., Dreschmann P., Weiland-Wascher A., Kern A. 809

Intrinsic bioremediation in the case of a diesel oil contamination at a railway yard: investigation and possible implementation
Staps J.J.M., Griffioen J., Kok A.P. 811

Purification of contaminated particulate material through chemical conversion
Peters B. 813

Groundwater risk assessment at a contaminated site based on integrating and spatially resolving investigations of groundwater pollutant concentrations and fluxes
Ptak T., Schwarz R., Teutsch G. 815

Evaluation of heavy metal mobility through the unsaturated zone of soil
Le Hécho I., Cornu S., Charbonnier P., Baranger P., Altmann S. 817

Natural attenuation of iron-complexed cyanides in soil and groundwater at former gaswork sites
Hommelgaard H., Munch S.K., Mosbæk H., Kjeldsen P. 819

Risk assessment of PAH in soil: behaviour and fate of non-extractable ^{14}C-PAH-residues under environmental stress conditions
Eschenbach A., Wienberg R., Mahro B. 821

The Ghent soil and waste treatment centre
Haemers J., van Hasselt J. 823

Characteristics of soils polluted by PAH
Barbé P., Lecomte P., Pazdej R. 825

Sampling and heterogeneity of polluted soils: the error assessment
Wavrer Ph., Lecomte P., Védrine H. 827

The Banisveld landfill: a research on natural attenuation and ecological effects
Slenders H., Van Vossen W., Kamsma T. 829

Study of transfer mechanisms of the residues in the soils of former manufactured gas plant sites
Delorme P., Carlier M. 831

Examination of mineral oil contaminated soils by means of thin-layer chromatography
Reimers Ch. 833

Comparison of *ex situ* and *in situ* biodegradation measurements for monitoring bioremediation
Haider I., Al-Saleh E., Henkler C., Fenwick C., Bär E., Henkler R., Mason J.R. 835

Metal pollution detected by infrared spectroscopy of contaminated soils
Dupuy N., Semmoud A., Maniez D., Sterckeman T., Huvenne J.P. 837

Contribution of *lux*-bacterial biosensors to remediation of BTEX contaminated land
Sousa S., Weitz H., Duffy C., Bär E., Henkler R., Anderson B.N., Mason J.R., Glover L.A., Killham K. 839

Problems arising from the lack of standardised methods for soil analysis
Pickard J.A. 841

Transfer of C_6H_6, C_2H_5OH, CCl_4 and water in non-isothermal soil
Globus A.M. 843

The potential threat to groundwater supplies from the fuel additive MTBE
Turrell J., Blackmore K. 845

First results of EXAFS-spectroscopy and SEM/EDX investigations on heavy metal contaminated soils as a tool for direct speciation analysis
Welter E., Calmano W., Mangold S. 847

Influence of organic pollutants on sorption of naphthalene in contaminated soils
Bayard R.M., Barna L., Gourdon R. 849

Long term metal release from deposits of municipal solid waste incineration (MSWI) bottom ash
Hirschmann G., Förstner U. 851

Managing C/N ratios in horse manure utilization systems
James R.E. 855

Solid-liquid partitioning of polycyclic aromatic hydrocarbons (PAH) in column experiments on harbour sludge
Keijzer Th.J.S., Middeldorp P.F., van Alphen M., Loch J.P.G. 857

Estimation of bias in the measurement of 'hot spots' on contaminated land
Squire S., Ramsey M.H., Gardner M.J. 861

Efficacy of large scale in-situ bioremediation treatment of a BTEX contaminated site regarding dissolution and degradation kinetics
Meier-Löhr M., Battermann G., Werner P. 863

Effect of metals on growth of field-derived soil bacteria
Mol S.N., Glover L.A., Henkler R.D., Anderson B.N. 865

Time-bombs effect in areas of the central Russia with high level of radionuclide contamination of soils
Golosov V.N., Ivanova N.N., Panin A.V. 867

Online measurement and sampling quality of soil vapor
Nahold M., Leest J. 869

Analysis of PAHs, hetero-PAHs (N,S,O), and N-substituted PAHs in tar oil contaminated soils including their degradation products
Meyer S., Steinhart H. 871

Distribution of CR and as in soils of an old tannery site and implications for future land use
Gerth J., Leberer A. 873

Sampling contaminated soil: how much should you take home?
Bunge R. 875

Physical remediation of the fine soil fraction by grinding attrition
Schricker B., Neeße Th. 877

The distribution of mineral oil pollutants on different particle size fractions
Dück J., Neeße Th., Breiter R. 879

Occurence and fate of plasticizers (phthalates) in soil: laboratory and field studies
Schiedek T., Grathwohl P., Einsele G. 881

Impact of diesel pollution on soil microbial activity and nematode communities
Jeffries R.A., Boag B., Neilson R., Crabb D., Wheatley R.E., Ritz K., Duncan H. 883

Groundwater contamination on small contaminated sites – remediation by sampling?
Petzold E., Tramm H., Veltrup D. 885

Hidden contaminated sites special treatment and financial aspects
Tramm H., Petzold E. 887

Prediction of bioavailabilty of persistent organic pollutants by a novel extraction technique
Reid B.J., Semple K.T., Jones K.C. 889

The use of environmental isotopes as leachate indicators in site investigation studies
Kissling O., Balderer W., Jordan P. 891

Aerobic degradation of hexachlorocyclohexanes in highly-contaminated soils from waste dumps of the chlorine-chemical industry
Riis V., Babel W., Miethe D. 893

Development of a validation protocol for methods of analysis of contaminated soil
Kibblewhite M., Heasman L., Forster V. 895

Leaching of inorganic constituents from contaminated soil
Ødegård K., Karstensen K.H., Lund W. 897

The use of microbiological indicators for the determination of the quality of soils: application to a covered hydrocarbon polluted site
Brohon B., Delolme C. 899

Quality assurance in the analysis of soils from land contamination
Forster V., Heasman L., Kibblewhite M. 901

Influence of soil characteristics on elimination of pentachlorophenol
Barančíková G., Gergel'ová Z. 903

A new approach for biomonitoring: assessing degradation potentials for polyaromatic hydrocarbons using gene probes
Meyer S., Moser R., Neef A., Stahl U., Kämpfer P. 905

Expert system for soil remediation
Ringeling R.H.P., Thomas A.G., Honders A. 907

In-situ bioremediation: increase of effectivity by the addition of humic acids
Kördel W., Klöppel H., Hund K. 909

Fiber-optic in-situ monitoring system for organic contaminants in water
Bürck J., Mensch M., Krämer K. 911

Soil pollution – mass spectrometry contribution in qualitative and quantitative approaches
Dudermel P.M., Dupeyron S., Couturier D. 913

Occurrence of polychlorinated dibenzo-*p*-dioxins and dibenzofurans as impurities in wood preservative contaminated and remediated soil
Kalevi K., Donner A., Kiviranta H., Vartiainen T., Jørgensen K.S. 915

Rapid procedures for the on-site measurement of polycyclic aromatic hydrocarbons in soils from former gasworks
Bennett A.M.A., Jones S.D., Morris R.S. 917

Biodegradation of methyl *t*-butyl ether by a mixed bacterial culture
Corcho D., Linton J.D., Watkinson R.J., Lerner D. 919

Chemical speciation of organic and inorganic compounds in municipal waste incinerator residues
Köster R. 921

Bacterial biosensors to screen *in-situ* bioavailability, toxicity and biodegradation potential of xenobiotic pollutants in soil
Ferguson Y., Shaw E., Glover L.A., Killham K., Meharg A.A. 923

Chromium contamination clean up using organic waste materials
Duncan H.J., Flowers T.H. 925

The fate of heavy metals in materials used for land reclamation
Fairley M.A., Farmer J.G., Paterson J.E., Pollard S.J.T., Rees R.M. 927

Stable isotopes as tracers of water flow and geochemical interactions relating to low-level radioactive waste disposal
Walker R.H. Graham M.C., Farmer J.G., Fallick A.E., Trivedi D. 929

The influence of microbial alteration of humic macromolecules on humic-actinide binding: implications for actinide mobility in soils
Vinogradoff S.I., Abbott A., Graham M.C., Farmer J.G. 931

Effect of temperature on toluene toxicity in psychrotrophic bacteria isolated or not from toluene polluted soil in a bioremediation perspective
Groboillot A., Philippe G., Chablain P.A., Truffaut N., Guespin-Michel J.F. 933

***In-situ* bioremediation of polynuclear aromatic hydrocarbons (PAHs) in gas manufacturing sites; possible role of indigenous and augmented bacteria**
Alsaleh E.S., Mason J.R. 935

Geochemical signatures of selected heavy metals in contaminated soils, stream sediments and alluvium associated to one case study of mining exploitation in Portugal
Santos Oliveira J.M., Ávila P.F. 937

Uptake of 2,4,6-trinitrotoluene in herbaceous plants
Scheidemann P., Sens C., Werner D. 939

Development of geochemical methods for the degradation of chlorinated organic contaminants in sediments – laboratory scale (Part 1)
Zoumis T., Calmano W., Förstner U. 941

Risk assessment methodology for small/medium scale groundwater contamination
MacDougall K.A., Fleming G. 943

Development of sampling strategies for the assessment of contaminated land
Harris M.R., Ferguson C.C. 945

The Scottish Contaminated Land Forum: sources of interlaboratory variability in the analysis of total metals in contaminated soil by commercial laboratories
Duncan H.J., Flowers T.H. 947

Kinetics of naphtalene biodegradation : determination of the kinetic and thermodynamic parameters
Collina E., Bestetti G., Ligorati R., Lasagni M., Pitea D. 949

Characterization of a contaminated site: principal component analysis as a tool to rationalize data heterogeneity
Lasagni M., Collina E., Pitea D. 951

The effect of organic matter composition on the interaction between PAHs and organic sorbents in soil
Schoone M., Schmidt M.W.I., Kögel-Knabner I. 953

Pb isotope signatures: evidence of origin and fluxes of heavy metals in an area polluted during 2000 years of Pb-Zn mining and smelting
Metzger R., Kramm U., Hoogewerff J., Baumann A. 955

The XUMA-GEFA knowledge-based system for the investigation and evaluation of contaminated sites in Baden-Württemberg and Saxony
Ferse W., Geiger W., Reißfelder M., Weidemann R., Reitz T. 957

Evaluation of bioremediation process efficiency: contribution of analytical, microbiological, molecular and ecotoxicological tests
Ducrocq V., Hallier-Soulier S., Pandard P., Thybaud E., Truffaut N. 959

Mobility of trace elements in soils and their transfer into crops
Podlešáková E., Němeček J. 961

Influence of soil texture on heavy metal mobilization in soils placed in zones with a semi-aridic climate
Martínez-Sánchez J., Pérez-Sirvent C., Vidal J., Gil M. 963

Cu, Sn and Ge mobilization in calcareous agricultural soils placed in zones with a semi-aridic climate
Pérez-Sirvent C., Martínez-Sánchez J., García-Rizo C. 965

The effect of soil compaction on seed emergence from an industrial solvent contaminated soil
Guerin T.F., Harrison A., Guerin P.M. 967

Hydraulic in-situ remediation techniques with surfactants: optimization of hydraulic systems
Josef R., Barczewski B., Koschitzky H.-P., Braun J. 969

Subsurface fate and transport of gasoline oxygenates
Bauman B.J., 971

The vertical migration of radionuclides in the soils after the Chernobyl accident
Kvasnikova E.V., Pegoev A.N., Stukin E.D. 973

Heavy metal contamination in urban soils
Bretzel F., Lubrano L., Petruzzelli G. 975

Speciation of nickel in natural and contaminated soils. Potentiality of phytoremediation
Barbafieri M., Lubrano L., Petruzzelli G. 977

Characterisation of heavy metals mobility in abandoned mining area in Sardinia (Italy)
Barbafieri M., Dadea C. 979

Development of methods to assess pollutant attenuation in geological barriers under landfill: optimizing procedures to investigate sorption; diffusion and colloid transport
Förstner U., Gerth J., Kammer F.v.d., Nordlohne L., Silla M., Weinberg R. 981

Investigation of *in situ* remediation alternatives for soils contaminated with high sulphates and heavy metals
Salami I.R.S., Anderson G.K. 983

Sampling strategies and analysis of soil samples
Falkenberg J.A. 985

Classification and soil quality monitoring; a case study
Mol G., Vriend S.P., van Gaans P.F.M. 987

Monitoring of kerosene infiltration in an unsaturated sandy soil at semifield scale in the Wageningen Rhizolab
Hwu C.S., Grotenhuis J.T.C., Malina G., Smit A.L., Groenwold J. 989

Potentials and barriers of heavy metals bioavailability in soil
Bielek P. 991

Influence of variable pore water velocity on the retardation of reactive solutes
Seuntjens P., Cornelis C., Nouwen J., Geuzens P., Verheyen R.F. 993

An in-situ biostimulation strategy for intractable shoreline sediments contaminated with diesel fuel
Peasley B.J., Guerin T.F. 995

Chromatographic measurement of adsorption isotherms on soil
Müller S., Struppe H.G., Ondruschka B., Remmler M., Roland U., Kopinke F.-D. 997

Photoacoustic spectroscopy: an attempt to characterize soils and sediments contaminated by PAHs
Cuypers M.P., de Leeuw R., Dóka O., Bicanic D., Grotenhuis J.T.C., Rulkens W.H. 999

Screening of groundwater toxicity downgradient of a landfill (Grindsted, Denmark) using a biotest battery
Baun A., Nyholm N., Bjerg P.L., Christensen T.H. 1001

Theme D: Risk assessment, quality and health criteria

Estimation of occupational polycyclic aromatic hydrocarbons (PAH) exposure of employees at a contaminated site: comparison with the predictions of three exposure models
Dor F., Empereur-Bissonnet P., Zmirou D., Dab W. 1005

Time-labelling soil remediation based on environmental and social-economic criteria
Beurmanjer C.A., de Boer C. 1007

Risk assessments on industrial sites as a pollution prevention method – the view of an insurance company
Gawlik M. 1009

A model risk assessment procedure for contaminated land
Harris M.R. 1011

Mapping the risks to human health from urban soils using geostatistical techniques
Nathanail C.P., Ferguson C.C., Browne M.J., Hooker P.J. 1013

Development of a rapid method for identification of pathogenic microorganisms by the polymerase chain reaction (PCR)
Theißen H., Schies U. 1015

Bulk waste management and risk assessment for large infrastructure projects
Guillaume B., O'Riordan N.J., Phear A. 1017

An innovative decision support system for quantitative risk assessment and clean-up objectives selection
Duong V.-L., Formisyn P., Bourgois J., Modolo R. 1019

In situ remediation of trace metals polluted soils: a fast physical chemical approach for the choice of amendments
Yousfi I., Bermond A. 1021

Practical experiences of risk assessment in Italy – opportunities arising from the forthcoming legislative framework
Chiampo A., Thomas A.O. 1023

Heavy metal contamination and soil microarthropods
Butovsky R.O., van Straalen N.M. 1025

A brief review of the use of risk assessment software for the characterisation of contaminated land
Plunkett J.S., Giles D.P., Langdon N.J. 1027

Towards quantitative risk assessment – a case history
O'Brien A.S. 1029

Release kinetics of 4-Cyanophenol from soil into cellulosic membranes
Arnold S.M., Bunge A.L., Guy R.H. 1031

Soil quality standards: a comparative study
Pitea D., Collina E., Lasagni M., Ligorati R. 1033

Quantifying the risk posed to groundwater from contaminated land – the ConSim model
Hall D.H., Harris R.C., Moncaster S., Plimmer B., Rogers M. 1035

Assessment of dermal exposure to soils
Kissel J., Garlock T., Shirai J. 1037

Earthworm avoidance test for soil assessment: alternative for acute and reproduction test
Hund K. 1039

Toxicity testing of polycyclic aromatic hydrocarbons with the rhizobium-legume symbiosis
Neumann H., Bode-Kirchhoff A., Wetzel A., Werner D. 1041

Effects of atrazine on maize litter decomposition and litter-bag microarthropods colonization in an experimental maize field
Cortet J., Poinsot-Balaguer N. 1043

Vlier-Humaan: a human exposure model embedded in Flemish legislation
Smit P.J., Goldsborough D.G. 1045

Toxicity of transuranic elements tested on earthworms
Viktorov A.G. 1047

Evaluation of the predictive capability of models of exposure to soil contaminants
Kissel J. Wawrukiewicz A., Bartell S., Shirai J. 1049

New biological and ecotoxicological methods to support risk assessment and soil remediation
Gruiz K., Molnár M., Szakács T., Bagó T. 1051

Theme E: Remediation and treatment technologies; research and development and proven technologies

---

Monitoring of clay-type surface barrier on dump sites
Brandelik A., Huebner C. 1055

Remediation of an industrial site contaminated with elementary white phosphorous at Bitterfield, Sachsen-Anhalt, Germany – exploration and realization
Neef U., Kotte G., Düresch R., Boehringer A., Böhme P., Bergmann V. 1057

Reclamation of polluted wet soils by solvent extraction
Nardella A., Sisto R. 1059

Investigation and operation of combined treatment and containment systems, 'Active containment', concepts and case histories
Jefferis S.A., Forster V. 1061

Guideline monitoring soil quality for industrial activities
Van Vossen W.J., Slenders H. 1063

Slurry trench cut-off walls: two years of results from the BG–BRE test site
Tedd P., Holton I.R., Wallace S., Daly P.J. 1065

Risk assessment, mass balance and successful remediation of a major gasoline spill in a residential area
Munz C., Gälli R., Kiayias G., Schmid B. 1067

Life cycle assessment method for remediation of contaminated sites
Volkwein S., Bender A., Klöpffer W., Hurtig H.-W., Battermann G., Kohler W. 1069

Cometabolic dechlorination of *cis*-1,2-Dichloroethene by ethene utilizing bacteria
Koziollek P., Bauer S., Bryniok D., Knackmuass H.-J., 1071

Groundwater treatment plant at the former gaswork remediation site 'Griftpark' in Utrecht, the Netherlands. The selection of a definite water treatment system
Pluim M.P., de Vries P.W., Oesterholt F.I.H.M., Appelman J.J.M. 1073

Treatment of contaminated soil and dredged harbour sludge by a new flotation approach
Mulleneers H.A.E., Bruning H., Koopal L.K., Rulkens W.H. 1075

Soil and groundwater research of the American Petroleum Institute
Bauman B.J. 1077

A case study of the remediation of soil contaminated with polychlorinated biphenyls (PCBs) using low temperature thermal desorption
Norris G., Al-Dhahair Z., Birnstingl J.G.A. 1079

BBT-sector survey soil remediation techniques
Gevaerts W., Pijls C., Dijkmans R., Dries V. 1083

Controlled and targeted mobilisation of copper in soil to enhance its accessibility for 'remediation-plants'
Wenger K., Gupta S.K. 1085

Enhanced vertical barriers for combined isolation and treatment
Evans J.C., Prince M.J. 1087

Risk-based selection of remedial measures for a shooting range area
Mroueh U.-M., Mäkelä E., Wahlström M., Olin M., Vahanne P., Liesivuori J., Kopponen P. 1089

Transfer of experimental measurands from the laboratory into the remediation practice – comparative investigations into the biological degradation of contaminants in fixed bed reactors and technical remediation windrows
Koning M., Hupe K., Lüth J.-C., Lubitz B., Stegmann R. 1091

Clean-up of heavy metal polluted soils: applicability and limitations of hydrometallurgical techniques
Thöming J., Stichnothe H., Calmano W. 1093

Remediation and rehabilitation of the Kuwait oil lake beds
Iwabuchi M., Kumamoto S., Shimizu Y., Asada M., Sueyoshi M., Takano Y., Al-Awadhi N., Balba M.T., Al-Daher R. 1095

An in-situ reactive barrier for the treatment of groundwater contaminated with trichloroethene: construction and operational performance
Thomas A.O., Haigh D.G., Roper M., Jefferis S.A., Norris G. 1097

Immobilization of soil: from co-disposal to beneficial use
van Leeuwen J.L.M., Pepels A.H.M. 1099

Thermal treatment of contaminated catcher-sand from firing ranges
Wevers H.H.A.G., Kramer Th.J. 1101

Off-site bioremediation of contaminated soil and direct reutilization of all soil fractions
Robra K.-H., Somitsch W., Becker K., Jernej J., Schneider M., Battisti A. 1103

Green soil clean-up by farmers: a challenge?
Leendertse P.C., Pak G.A. 1105

Air and contaminant migrations in groundwater induced by in-situ air sparging
Hirata T., Egusa N., Fukuura K., Matsushita T. 1107

Assessment of soil quality using a multitiered test battery of bioassays
Bierkens J., Klein G., Corbisier P., Van Den Heuvel R., Verschaeve L., Weltens R., Schoeters G. 1109

Soil remediation by metal-accumulating plants: how to monitor the success of remediation
Keller A., von Steiger B., Kayser A., Schulin R. 1111

Integrated long-term management of radioactively contaminated land: the Ceser Project
Salt C.A., Rekolainen S. 1113

Stabilisation of highly polluted soils
Kontopoulos A., Theodoratos P. 1115

The feasibility of *in situ* bioremediation of groundwater nitrate
Cartmell E., Clark L., Oakes D., Smith S., Wheater H. 1117

Phytoremediation of heavy metal contaminated sites by potential fibre crops
Kerr J., Pulford I., Duncan H., Wheeler C. 1119

A comprehensive evaluation on the use of oxygen release compound in bioremediation
Koenigsberg S.S. 1121

Decontamination of mercury polluted soils by electroleaching: assessment of the ecological clean-up benefit
Thöming J., Franke S. 1123

Treatment of hydrocarbon contaminated groundwater based on hydrological tests
Szabó. P., Nagy G. 1125

A model procedure for evaluation and selection of remedial measures for contaminated land
Smith M.V. 1127

Recommendations on quality criteria for remediation of contaminated sites
Mroueh U.-M. 1129

Treatment of contaminated soils DFG – research centre SFB 188
Stegmann R. 1131

Remediation of contaminated residue from the chlor-alkali industry with elemental mercury, by using an electrolytic process
Sobral L., Thöming J. 1133

Assessment of properties improvement of cement-based solidified dredged sludge
Boutouil M., Levacher D. 1135

Removal of heavy metals from contaminated soils by complexing agents
Kiefer R., Höll W.H. 1137

In situ attenuation of heavy metal mobility in contaminated soil by the use of paper mill sludge
Petruzzelli G., Barbafieri M., Bretzel F., Pezzarossa B. 1139

Clean up of polluted soil – environmental/economic evaluation and optimising of in-situ techniques
Deigaard L., Nielsen S.T. 1141

Hydrocarbons contaminated soil remediation using soil venting. Application of simulation models
Bonilla A., Cuesta P., Zubiaga R., Hierro B. 1143

Willow clones for short rotation coppice on heavy metal contaminated land
Pulford I.D., Riddell-Black D. 1145

Index for beneficial use on soils (IBUS)
James R.E. 1147

Biological removal of wood preservative (PCP) wastes in soil. Autochthonous microflora and effect of compost addition
I. Gorostiza, Susaeta I., Bilbao V., Díaz A.I., San Vicente A.I., Salas O. 1149

Recovery of HCH (Hexachloroclohexane) contaminated soils using solvent extraction technologies
Salas O., Sagarduy M., San Vicente A.I., Díaz A.I., de la Quintana E., Susaeta I. 1151

The use of cost benefit analysis in selecting remedial options for contaminated land
Martin I., Lowe M., Herbert S. 1153

Application of the biofertilizer made of the products of aerobic treatment of the waster waters from the pig-farms in the monitoring system of antropogenic soils of Northern Czechia
Barbolina I.I., Arkhipchenko I.A., Vana J. 1155

Decrease in the soil pollution in animal breeding industrial areas using the methods of microbial ecotechnology
Arkhipchenko I.A., Alekseyev M.A. 1157

Defining the radius of influence in a biosparging pilot test
Buzzelli M., Gavinelli M. 1159

Electroextraction of heavy metals by electomembrane process
Hassen-Khodja D., Persin F., Sandeaux J., Sandeaux R., Gavach C. 1161

Support of the efficient handling of contaminated sites by the AlfaWeb information system
Geiger W., Reißfelder M., Weidemann R. 1163

Investigation and remediation of a solvent spill on the chalk outcrop of Southern England
Blackmore K., Clark L., Sims P. 1165

The sequential extraction of metal forms in the soil of the Beskid Zywiecki in Poland
Nowak B., Siobowicz G., Lukasik K., Soltysiak G. 1167

Assisterix – a TNO software product for soil protection at industrial sites
de Weger D. 1169

Decision support system for soil protection of industrial sites
de Weger D. 1171

REC: a decision support system for comparing soil remediation options based on risk reduction, environmental merit and costs
Nijboer M.H., Okx J.P., van Drunen M.A., Janssen R. 1173

Confinement techniques for contaminated topsoil
Mikheikin S.V., Alekseev A.N., Pronina L.V., Smirnov A.Yu. 1175

Effect of mechanical stress on microbial soil remediation in solid-state-bioreactors
Scholz J., Müller B.G., Schwedes J., Deckwer W.-D. 1177

Feasibility of decontamination of lead-polluted soil by aqueous sodium chloride and sodium humate solutions
Tütem E., Apak R., Güçlü K., Hizal J. 1179

Centrifuge modelling of self-weight of contaminated or partially contaminated dredged sludges
Levacher D., Marot F., Conil P., Boutouil M. 1181

Soil vapor extraction: test and control
Johannsen J., Petzold E., Thimm A. 1183

Remediation of groundwater and aquifer material at the RHO oil refinery, with particular reference to the use of *ex situ* bioremediation
Turrell J., Clark L., Berbenni P., Nobili F. 1185

Laboratory and field pilot evaluation of co-metabolic bioventing for the remediation of soil contaminated with trichloroethene (TCE) and trichloroethane (TCA)
Morgan P., Sayles G.D., Moser L.E., Gannon D.J., Kampbell D.H., Franz T., Vogel C.M., Major D.W., Bell M.J., Holmes M.W. 1187

Development of a bioreactor process for treatment of PAH contaminated soils
Sobisch T., Niebelschütz H. 1189

Regional effectiveness of contaminated site remediation activities
Schwarzenbach R.C., Heitzer A., Stäubli B., Scholz R.W. 1191

Decision support system for treatment of dredged sediments
Joziasse J., Bakker T., Eggels P.G. 1193

The treatment of aquifers contaminated with arsenic, zinc and cadmium by the bipolar electrolysis technique: the overpelt project
Pensaert S. 1195

The use of methylene urea as nitrogen fertilizer in oil-waste landfarming
Peltola R., Turpeinen R., Koivunen M., Kähkönen L., Salkinoja-Salonen M., Romantschuk M. 1197

Remediation of tetrachloroethene-contaminated groundwater at a site in Northern England
Blackmore J. 1999

***In situ* immobilization of heavy metals in contaminated soils: effects on plants and earthworms**
Oste L.A., Schröder T.J., Bakker S., Oppenheimer M., Lexmond Th.M. 1201

Directed microbial manipulation in an artificial groundwater/sand aquifer system using an electrical current
Dearlove J.P.L., Abbott A., Rigby C. 1203

Low cost incineration residues detoxification process
Lee P.H., Nasserzadeh V., Swithenbank J., McLeod C., Goodfellow J. 1205

Potential use of β-cylodextrin for bioremediation of contaminated soil
Molnár M., Gruiz K., Fenyvesi E, Szönyi M. 1207

Theme F: Land reuse, legal and financial development, management of contaminated land

The vegetation of covers for landfills and contaminated sites: monitoring data and recommendations
Sokollek V., Seelig-Braker A. 1211

Training needs for contaminated land specialists
Nathanail P., Nathanail J. 1213

Financing remediation of contaminated sites in Austria
Steirer T. 1215

Assessing the durability of building materials in contaminated land
Garvin S.L., Ridal J.P., Halliwell M. 1219

Exhaustive control of a construction project in contaminated soil
Travesa F., Colomer V., Rius J., Mundó B. 1221

Monitoring the reclamation of acidic spoil for amenity woodland
Heal K.V., Salt C.A., Grieve I.C., Hipkin J.A. 1223

Utilising contaminated and disturbed industrial land for short rotation coppice
Rees S., Pulford I.D., Duncan H.J. 1225

Financing the remediation of contaminated sites
Lowe M., van Sandick O., Salter R. 1227

The relocation of a football stadium onto a closed landfill
Braithwaite P.A., Wright P.D. 1229

Country sessions

Germany

Country session Germany
Holzwarth F., Franzius V. 1233

Framework for contaminated sites management in Germany
Bieber A., Franzius V., Freier K. 1235

Contaminated military sites: German experiences
Szelinski B.-A. 1237

Requirements for contaminated sites cleanup within the framework of derelict land recycling
Freier K., Reppe S. 1241

Financing clean up of contaminated sites in the new Federal States
Sanden J. 1243

Research and development: 'contaminated sites remediation technologies'
Hübenthal K.-H., Wittmann U. 1245

***VEGAS*: a research facility for subsurface remediation at the University of Stuttgart and a research framework**
Koschitzky H.-P., Barczewski B. 1249

Switzerland

Soil pollution prevention and contaminated site management in Switzerland
Wenger C., Dettwiler J., Philipp R., Vallat Ph., Munz C., Kyas A., Jaggy M. 1253

Basque Autonomous Community

New developments in contaminated sites policy in the Basque Country
Larrañaga E., Ortiz R., Epelde J., San Martín J., Muguruza I., Holzwarth W., Zárate G., Sagarduy R., Aurrecoechea J.L., Alvarez A., Galera J., Martín I., Blázquez J.C., San Jorge R., Camiña I. 1263

Finland

Finland country session
Seppänen A., Puolanne J., Kukkamäki M., Huttula P., Kalevi K., Puhakka J., Tuomainen J., Pyy O. 1273

Technical tour

Contamination assessment technologies and remediation decision making at a former refinery site
Lambson M.D., Syratt W.J. 1289

Index of keywords xxv

Index of authors xxxv

Theme A:
International cooperation

EXPERIMENTAL AND THEORETICAL STUDY OF THE EFFECT OF PRESSURE ON THERMAL DECONTAMINATION OF SOILS POLLUTED BY HYDROCARBONS

V. Risoul[1+2], G. Trouvé[1] and P. Gilot[1].
[1] Laboratoire Gestion des Risques et Environnement, Univ. de Haute Alsace, 68200 Mulhouse, France
2 TREDI, Departement recherche, BP 184, 54505 Vandoeuvre lès Nancy, France

Key words : Soils decontamination, hydrocarbons, vacuum, modelling.

EXPERIMENTAL

The thermal decontamination of three different soils, clayey (S1), calcareous (S2) and sedimentary (S4), which were artificially polluted (3%) by naphthalene, hexachlorobenzene (HCB) or 4-chlorobiphenyl, was studied using thermogravimetric analysis (TGA) at different pressures ranging from 10^4 Pa to 10^5 Pa. Small samples of around 30 mg of contaminated soils were placed in the crucible of a Cahn thermobalance and heated at 5°C/min under an air flow (5Nl/h). The weight loss was recorded during the decontamination process. The same experiments were carried out with non contaminated soils to give the weight loss due to the soil itself. Thus, the extent of contaminant removal could be determined as a function of temperature (20-450°C).

RESULTS

The TGA experiments returned different quantities such as the maximum decontamination rate and its corresponding temperature, and the decontamination domains defined as the temperature ranges for which the decontamination rates are higher than one tenth or half the maximum rate, respectively. These quantities are presented in Table 1, together with the boiling points of the contaminants at the operating pressure, for comparison. Maximum decontamination rates significantly increased with decreasing operating pressure although the corresponding temperatures were reduced by roughly 20-50°C, except for soil S1. The total temperature ranges of decontamination were also shifted towards lower temperatures by 20-50°C.

MODELLING

A model [1], developed to predict the extent of decontamination versus temperature during TGA experiments under 10^5 Pa, was adapted to be used in the case of the reduced operating pressures. This model, based on the evaporation of the contaminant, returned good predictions under reduced pressures, except for the clayey soil S1 for which evaporation is not the relevant mechanism for contaminant removal, whatever the pressure. This model showed that the contaminant diffusivity (proportional to the reciprocal operating pressure) is the parameter responsible of the 20-50°C shift returned by the experiments.

This model appears to be a very useful tool to quickly predict the temperature range of decontamination under a given total pressure, for a given set contaminant-soil.

Contaminated Soil '98, Thomas Telford, London, 1998, 719–720

Table 1 : Maximum decontamination rates (r_{max}) and decontamination temperature ranges returned by TGA.

Pressure (P) (Pa)	r_{max} (mg/s)	Temperatures (°C) corresponding to r_{max}	Temperature ranges (°C) where $r > 0.1r_{max}$	Temperature ranges (°C) where $r > 0.5r_{max}$	Boiling points (°C) at the corresponding P
	S1	**POLLUTED**	**BY**	**HCB**	
10^4	8	215	70-300	145-240	237
$5x10^4$	5.5	215	70-310	175-270	282
10^5	2.5	210	70-360	180-310	309
	S2	**POLLUTED**	**BY**	**HCB**	
10^4	18	168	135-195	100-180	237
10^5	16	190	165-220	135-210	249
	S4	**POLLUTED**	**BY**	**HCB**	
10^4	24	140	95-190	115-155	237
$2x10^4$	23	146	95-180	120-165	249
$5x10^4$	20	174	110-220	150-185	282
10^5	19	184	130-215	155-200	309
	S4	**POLLUTED**	**BY**	**4-CHLOROBIPHENYL**	
10^4	15	85	50-150	50-130	198
$5x10^4$	12	110	60-180	60-160	255
10^5	9	110	50-220	90-180	290
	S4	**POLLUTED**	**BY**	**NAPHTHALENE**	
10^4	7	35	25-110	25-50	129
$5x10^4$	6	37	25-125	30-65	173
10^5	4	55	25-135	35-70	218

CONCLUSION

Decreasing the pressure from 10^5 to 10^4 Pa increased the decontamination rates and significantly increased the extent of decontamination at a fixed temperature. TGA appears to be a very convenient technique to investigate the feasibility of a thermal treatment at a given pressure. A model is also available to predict the thermal behavior of a polluted soil at a given pressure.

REFERENCES

[1] Gilot, P., Peters, W.A. and Howard, J.B. (1997) *Environ. Sci. and Technol.* 31 (2), 461-466.

ACKNOWLEDGMENT

We thank TREDI and the french « Ministère de l'Industrie » for the financial support of this work. M. G. Fraysse, who designed the pilot, is particularly acknowledged.

THE SCOTTISH CONTAMINATED LAND FORUM (SCLF): A COLLABORATIVE APPROACH TO CONTAMINATED LAND ASSESSMENT

Simon J.T. Pollard[1*], John Gould[2] and Hugh Flowers[3]
[1] Scottish Environment Protection Agency, Head Office, Erskine Court, The Castle Business Park, Stirling, Scotland, FK9 4TR, UK
[2] Scottish Enterprise, 120 Bothwell Street, Glasgow, G2 7JP, UK
[3] Department of Chemistry, University of Glasgow, Glasgow, Scotland, G12 8QQ, UK

Key words: regeneration, education and training, reuse, environmental investigations

Introduction

Scotland is internationally recognised as having a developed skill base in the management of land contamination. Recent (1996) estimates[1] of brown field land indicate some 13 721 hectares (ha) of 'vacant' (8 788 ha) and 'derelict' (4 944 ha) land, representing nearly 5 700 sites across Scotland in similar proportion between the public and private sectors. Whilst this represents approximately only 0.2% of the total land area of Scotland, its concentration (44% of all sites) in the four local authority areas of the populated 'central belt', together with a potential increase in demand for 323 200 new homes in Scotland over the next 10 years, makes the rehabilitation and reuse of such land an important policy issue.

Progress to Date

The management of contaminated land necessarily brings together a number of conflicting interests that can often threaten delivery of a successful solution for all parties. Discussions during sale and purchase of contaminated land on the origin and transfer of environmental liabilities frequently revolve around the credibility of site investigation reports and of the supporting analytical data and risk assessment. With the objective of addressing these difficulties, the Scottish Contaminated Land Forum (SCLF) was formed in 1995 to bring together private and public sector organisations in Scotland with an interest in developing and enhancing best practice principles in the assessment, development and utilisation of contaminated land in Scotland. SCLF has a strategic vision of '*encouraging and promoting the effective and sustainable rehabilitation and re-use of contaminated land in Scotland and elsewhere through the knowledge and skills of Scottish-based professional services and businesses; and to thereby positively contribute both to the future growth of the Scottish economy and the quality of life of its people and communities*'.

SCLF offers an open platform for discussion on key aspects of contaminated land assessment outwith the constraints of commercial contracts. Membership (116 at present) includes environmental consultants, laboratory professionals, planners, environmental health officers, environmental regulators, funders, developers, solicitors, insurers, contractors and landowners. The affairs of the SCLF are managed by an elected executive group and its research activities are conducted by working groups established from the membership. To date, SCLF has:

- developed a constitution in close consultation with its membership;
- organised a regular series of Forum meetings covering the legislative, practical and policy aspects of contaminated land management;
- prepared and adopted a 5-year business plan with 10 strategic objectives, goals and targets

* current address: Risk Analysis Manager, National Centre for Risk Analysis and Options Appraisal, Environment Agency, Steel House, 11 Tothill Street, London, SW1H 9NF

Contaminated Soil '98, Thomas Telford, London, 1998, 721–722

for 1997-2002;

- adopted and disseminated two publications as examples of best practice within the industry: 'How to Investigate Contaminated Land' (requirements for contaminated land site investigations); and 'How to Approach Contaminated Land' (a framework for the assessment of contaminated land and the selection of remedial options);
- initiated work on a new best practice manual: 'How to Analyse Contaminated Land';
- established a series of working groups addressing key items such as:
  - the assessment of waste contaminated soil with reference to the UK Special Waste Regulations, 1996 (that implement Council Directive 91/689/EEC on Hazardous Waste); and
  - the analysis of complex hydrocarbon-contaminated soils; and
- established and operated a comprehensive inter-laboratory testing group comprising 17 commercial laboratories operating in Scotland.

These activities have provoked wide discussion amongst the membership with key items being (i) the professional standards required of laboratories and environmental consultants and the need for confidence between these communities in each others' work; (ii) the role of risk assessment procedures in the management of contaminated land; (iii) issues of uncertainty in analytical measurement; (iv) the capabilities of individual analytical procedures for complex organics; and (v) the new UK legislative framework being introduced by Part IIA of the Environmental Protection Act 1990.

Operation of the inter-laboratory testing programme has raised a number of established issues surrounding consultant-laboratory relationships including:

- chain of custody issues (sample delivery and preparation);
- the construction and selection of analytical suites;
- the varying capabilities of analytical methods and individual laboratories;
- data reporting and interpretation; and
- the use of chemical data in land quality statements.

Initial work in the testing programme has centred on a round robin scheme for the analysis of heavy metals in contaminated soils. This has been used partly as a proficiency scheme but has also allowed the group to carry out experimental work to investigate sources of variation between members of the group. Levels of variability are comparable with those in larger proficiency testing schemes such as the UK 'CONTEST' scheme. The detailed evaluation of the results of the group and exchange of ideas has to a large extent overcome concerns of commercial confidentiality and is leading to a better understanding of the sources of analytical variability within a commercial context which will lead to greater consistency in the results provided by Scottish laboratories. Active discussion of the results of the programme has resulted in two central objectives for the future that reflect the collaborative approach adopted amongst the membership: (i) the promotion and development of Scottish analytical expertise within the estimated £4.5 million contaminated land analytical market; and (ii) the development and expansion of an acceptable analytical protocol for the assessment and development of contaminated land.

SCLAF can be contacted through the Secretary at: The Scottish Contaminated Land Forum, c/o EnviroCentre, Woolfson Centre, 106 Rottenrow East, Glasgow, G4 0NW, UK, Tel: +44 (0)141 553 4128; Fax: +44(0)141 553 4186

[1] The Scottish Office (1996) Statistical Bulletin, Vacant and Derelict Land Survey, 25pp, ENV/1996/4

SOIL MANAGEMENT IN EUROPEAN PORTS

Ammerlaan, R.A.[1] and Engelhardt, D.[2]

[1] Public Works Rotterdam, P.O. Box 6633, 3002 AP Rotterdam
[2] Rotterdam MUnicipal Port Management, P.O. Box 6622, 3002 AP Rotterdam

Keywords: authorities, clean-up cost, clean-up technologies, guidelines, industrial areas, on-site treatment

ECEPA (Environmental Challenge for European Port Authorities) has estalished a platform of European Ports collaborating on environmental issues on the basis of specific projects. The underlying idea of ECEPA is to find a possibility for ports to invest in environmental measures without losing their competitive position. ECEPA is linked to the Environmental Committee of ESPO (European Sea Port Organisation).

Many European Ports face soil pollution problems and the possible high costs involved in its remediation. Nine ESPO and ECEPA member ports therefore started the project "Soil Recycling in European Ports" to find new ways to handle the soil pollution problem in a financially acceptable manner. The ECEPA-project's main goal was to develop, demonstrate and exchange low cost soil cleaning techniques and soil policy approaches. The ports of Amsterdam, Rotterdam and Antwerp were selected as pilot ports, and Barcelona, Copenhagen, Dublin, Göteborg, Le Havre and Pireaus as observers (see figure 1). This project was co-funded by the Life Programme (EC-DGXI) and has been finalized recently.

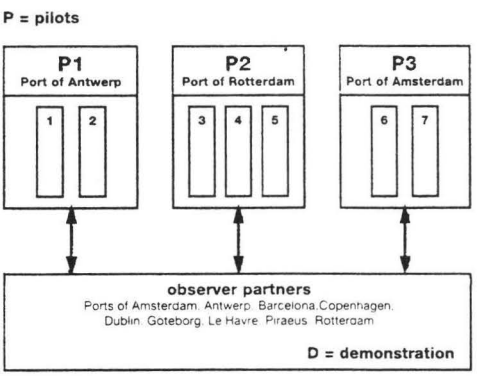


Figure 1 Project organisation.

The findings of pilot projects and workshops have resulted in a guideline 'Soil Recycling in European Ports'. The guideline offers - on general and technical port management aspects - 10 checklists (see figure 2). The checklists give answer on the

question how to proceed as a port authority facing the situation of polluted sites and on anticipating potential pollution problems. A general information sheet about the project and nine fact sheets about the pilots are included in the guideline.

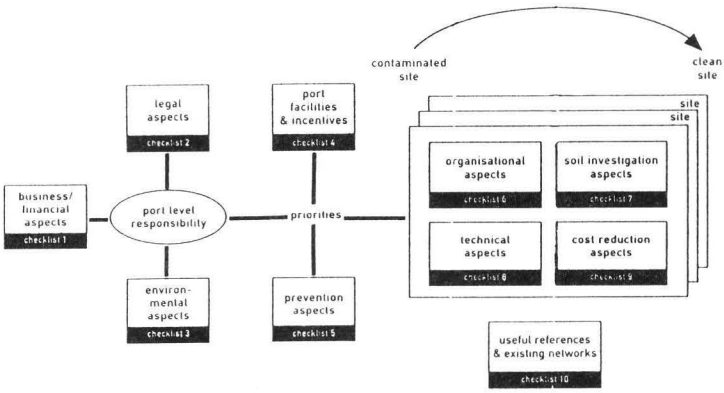


Figure 2 Structure of the guideline.

As part of the demonstration project of Rotterdam, the Port of Rotterdam built the TOP-Europoort, a temporary storage and testing facility in the middle of the port area. On this testing facility two demonstration projects were carried out. The Technical University of Delft demonstrated a physical process using linked separation units. Some of the units were innovative. This demonstration has given the observers a better insight in the possibilities and costs of (mobile) physical processing of contaminated soil. Caldwell Environmental Netherlands demonstrated on-site landfarming with the use of additives, four batches of 250 - 700 tons were tested, contaminated with mineral oil and PAH and, has given the observers a better insight in the costs and the possibilities of the method.

Heidemij (now called Arcadis) demonstrated a separation process using their mobile installation. The fine separation residue was used to test the potential of bioremediation by landfarming. Landfarming of residues is promising as long as the non biodegradable parameters in the residue stay below beneficial reuse value. Public Works of Rotterdam has set-up a guideline for (environmentally) efficient handling of ashes and slags. The port of Rotterdam has a twofold interest related to ashes and slags, because they are found during reconstruction and remediation works and because the can be used in infrastructural works.

The Port of Antwerp has carried out a pilot test with horizontal drains and has set-up a total cleaning plan for an industrial site in their port. The Port of Amsterdam demonstrated an on-site landfarming project and an aeration test. As a result of this international project the participants of both the pilot ports and the observer ports have a better understanding of handling (potential) soil problems and can use the guideline and the other reports to transfer the knowledge in their own organisation.

KNOWLEDGE TRANSFER TO EASTERN EUROPE: LEARNING BY EXPERIENCE

D.G. Goldsborough and P.J. Smit

Van Hall Instituut, PO Box 17, 9700 AA Groningen, The Netherlands

Keywords: Knowledge transfer, authorities' role, contractor responsibility, data analysis, legislation, environmental management, environmental investigations, case study

With the fall of the Iron Curtain and the disintegration of communist regimes in Eastern Europe interest from the West in this region has grown considerably. One of the key issues has been -and still is- dealing with environmental problems. Tackling serious diffuse and local soil contamination in Eastern Europe is an environmental issue that receives considerable attention. Since 1993 the Van Hall Instituut has been involved in several projects aimed at knowledge transfer from the West to the East. Our involvement in knowledge transfer falls into four categories: offering training courses, presenting papers , demonstrating software and participating in projects (Aquatest, 1996) and (Dusilek & Shore, 1995). Chronologically our activities were carried out in the Czech Republic, former East Germany, the Slovak Republic and Poland. In this paper positive and negative aspects of our involvement in the four mentioned categories are discussed. Two case studies carried in collaboration with partners in the Slovak Republic (Brtanova et al. 1996) will be discussed to illustrate success and failure factors.

Besides the inevitable management problems, e.g. lack of money and clear objectives, involved in international projects, we frequently encountered communication and expertise problems.
Major communication problems could almost always be traced back to language problems, translation problems (e.g. lack of an experienced translator) and 'getting into touch' problems. In our view most expertise problems that we encountered were mainly caused by a lack of integral problem solving capabilities. Although we found that the available expertise on specific topics, e.g. geology and chemistry, was on a very high level, very few people were able to combine expertise from different fields, available data and tools, to solve soil contamination problems effectively.

Based on the lessons we have learnt over the years we have several tips for effective knowledge transfer from the West to the East. The most important recommendations for the four mentioned categories are mentioned below.

Training courses in English can best be organised on location and not in the West. If lecturers are proficient in the language of the country were the course is offered than it should be offered in that language. If courses can only be offered through the mediation of a translator one should strongly rethink offering them. Presenting papers at conferences or meetings in Eastern Europe can be very rewarding, but plan to hang around to discuss your work with interested parties during or shortly after the meeting. Don't expect to be contacted frequently via mail, fax, etc. when you are back based only on your presentation! Demonstrations of software used for problem solving, e.g. a human exposure model or a transport model, can greatly enhance the communication

process. Many people find looking at numerical and graphical representations of a problem very enlightening, this in contrast to verbal communication. Successfully participating in projects in collaboration with partners from Eastern European countries firstly depends heavily on establishing the qualifications of all involved and secondly on agreeing on the objectives of the project. From these two points it is relatively easy to determine who does what, who is responsible for what, how much time each activity should take, etc.

Although fantastic new media for communicating long distance: e-mail, fax, phone, etc. are currently available for virtually everyone, one should not rely on these media too heavily. When you really need to solve problems it's best to do this on location and in person. Besides social, cultural and psychological advantages, face-to-face contact offers extra options compared to long distance communication: the ability to draw, calculate options and explain issues at length.

References

Aquatest (1996). *Proceedings of the Third International Workshop on Contaminated Land.* April 1-3, Prague, Czech Republic.

Brtanova, D., Matiova, Z., Goldsborough, D.G., Smit, P.J. (1996). *Application of the Dutch Human Exposure Model RISC-HUMAN to Slovak Conditions and Legislation with Respect to Risk Assessment.* In: Warsaw 1996, Third International Symposium and Exhibition on Environmental Contamination in Central and Eastern Europe, Warsaw, Poland, pp. 504-506.

Dusilek, P. & Shore. M. (Eds.) (1995). *Proceedings of the Dutch-Czech Workshop on Risk Assessment for Contaminated Sites and Target Levels for Clean-up.* February 13-14, Prague, Czech Republic.

RTDF BIOREMEDIATION OF CHLORINATED SOLVENTS CONSORTIUM

M J Bell (ICI Chemicals & Polymers Ltd., P O Box 13, Runcorn, Cheshire, WA7 4QF, UK)
D E Ellis (DuPont Company, P O Box 80027, Wilmington, DE 1988-0027, USA)
D J Gannon (Zeneca Corp., Sheridan Park Environmental Laboratory, 2101 Howden Road, Mississauga, Ontario, L5K 2L3, Canada)
G M Klecka (Dow Chemicals Company, Building 1803, Midland, MI 48674, USA)
J Licarta (Novartis Corp., P O Box 18300, Greenboro, NC 27419, USA)
D T Meiers (Idaho National Engineering Laboratory, P O Box 1625, Idaho Falls, ID 83402, (USA).
D W Major (Beak Technologies Inc, 42 Arrow Road, Guelph, Ontaria, N1K 1S6, Canada)
J J Salvo (General Electric Company, P O Box 8, Schenectady, NY 12301 0008, USA)
G D Sayles (US Environmental Protection Agency, National Risk Management Research Laboratory, Cincinnati, OH 45268, USA)
C M Vogel (US Air Force, AL/EQWOL, 139 Barnes Drive, Suite 2, Tydall AFB, FL 32403-5323, USA)
R Woodworth (US Air Force, AL/EQW-OL, 139 Barnes Drive, Suite 2, Tydall AFB, FL 32403-5323, USA)

This poster describes the organisation and mission of a very successful public-private partnership which is a useful model for similar activities elsewhere.

The Bioremediation of Chlorinated Solvents Consortium is one of five Action Teams of the Remediation Technologies Development Forum (RTDF). The consortium was established in 1993 when representatives from six companies, the US Environmental Protection Agency (EPA) and the Department of Energy (DOE) met to discuss their mutual interest in developing *in situ* bioremediation technologies to degrade chlorinated solvents in soil and groundwater. The original industrial partners of he Bioremediation Consortium (DuPont, Dow, General Electric, Monsanto, Novartis, and Zeneca) were later joint by two more: ICI and Beak International.

The industrial partners signed a research agreement in 1994 and agreements were then negotiated with the EPA, the DoE and the US Air Force (USAF) to facilitate collaboration between the public and private sectors on the planned research projects. These legal arrangements were time-consuming but have proved flexible and practical. There is a mechanism for sharing proprietary technology such that consortium members can use shared or developed technology at their own sites.

The rationale for creation of this consortium (and of the RTDF initiative as a whole) was to enable the efficient leverage of resources for technology development and implementation in a non competitive area for the problem holders. This has enabled

Contaminated Soil '98, Thomas Telford, London, 1998, 727–728

elimination of duplication of effort and collaboration on a defined work plan for the common good. Key elements of the work processes include a resource commitment: members must commit approximately one person year per annum of in-house effort over four years and support some field work. A steering committee on which all of the members are represented provides policy and ratifies technical strategies. A technical conference is held once per year and ad hoc technical groups met regularly. The total cost of the work-plan is currently forecast to be US$ 16 million.

The mission of the Consortium is to accelerate the development of the most cost-effective *in situ* bioremediation processes for degrading chlorinated solvents. To accomplish this mission, Consortium members jointly participate in the research, development, demonstration, evaluation and dissemination efforts necessary to achieve public and regulatory acceptance of these biological processes. Consortium members contribute personnel, equipment, laboratory facilities and funding needed to complete the mission.

The Consortium focuses on three in situ bioremediation processes: cometabolic bioventing (for treatment in the vadose zone), intrinsic bioremediation (for treatment of large ground water plumes) and accelerated anaerobic bioremediation (for treatment of concentrated areas within plume). Each technology is being demonstrated at two sites. The first site for all three technologies has been Dover Air Force Base, Delaware, USA and work here will be complete in 1998. The second site for testing is being selected now.

Extensive geological and hydrogeological characterisation work at all sites has provided significant insights into subsurface conditions. These data and laboratory biodegradation studies and microbial characterisation work have supported the subsequent field work. Mathematical computer models have been and continue to be developed to enable performance prediction at other sites.

It is the intention that all of the work performed will be published in the scientific literature. Already, information can be accessed readily on the World Wide Web (http://www.rtdf.org).
Other papers presented to this conference provide a comprehensive progress report to date.

A training course to raise awareness and understanding of natural attenuation has been developed by the Consortium in collaboration with the Interstate Technology and Regulatory Co-Operation Workgroup (ITRC) of the Western Governors Association. The primary audience for the course is regulators and other professions working with contaminated land. The course has been delivered to a number of groups across the USA and it is planned to make this available to interested parties in Europe. Also, a document entitled "Natural Attenuation of Chlorinated Solvents: Principles and Practices" has been developed to assist in providing information in the natural attenuation of chlorinated solvents and its assessment. This document can be downloaded from the Web site.

THE AMSTERDAM QUESTIONNAIRE

Authors: W. Visser[1], E. Elkenbracht[1], I. Martin[2], S. Johnson[3] and P. Bardos[4]
[1] Tauw Milieu, P.O. Box 133, 7400 AC Deventer, The Netherlands
[2] Environment Agency, Olton Court, 10 Warwick Road, Olton, Solihull, B92 7HX West Midlands, United Kingdom
[3]A&S Associates, 79 Tilmore Gardens, Petersfield, GU32 2JA Hants., UK
[4]R[3] Environmental Technology, P.O.Box 58, Ware, Hertfordshire SG12 9UJ, UK

This poster was prepared for the Dutch Ministry of Housing, Spatial Planning and Environment on behalf of the *Ad Hoc* International Working Group on Contaminated Land

Keywords: contaminated sites, international cooperation, policies, liability, risk management, , soil protection, soil remediation, sustainable soil use.

The initiative

The Amsterdam Questionnaire is an initiative of the *Ad Hoc* International Working Group on Contaminated Land, which is an informal forum for international cooperation and exchange of experiences and information on contaminated land policies and implementation of these policies *(see accompanying poster)*. The Group was established in 1993 and by 1998, 30 countries and international organisations participate in the Group, covering all continents and all stages of policy development.
The idea for a questionnaire reflects the spirit of the purpose of the Group: The Questionnaire was designed to provide basic information across all countries participating, and serves as a reference source. It is used to identify similarities and differences in policy issues, areas for future discussion, analysis and information exchange and to help target future survey work on specific contaminated land topics.

Nature and scope of the questionnaire

The first questionnaire was circulated among the participants of the first meeting of the Group and became known as the Vienna Questionnaire. At the second meeting of the Group, the report of the analysis of this questionnaire was regarded as a valuable working document, and the need for an updated questionnaire was expressed. This became the Amsterdam Questionnaire. The following aspects of contaminated land policies are covered in the Amsterdam Questionnaire:

1. Overall policy and legislation, including liabilities and funding;
2. Information, assessment and prioritisation;
3. Remediation technologies.

Development and application of remedial technologies: an example of the results

The issue of availability and application of different remedial strategies both now and in the next 5-10 years has, among other things, been investigated in the Questionnaire. The estimated use of remedial options resulted in a clear picture on this issue, referring to six different remedial strategies: see figure 1.

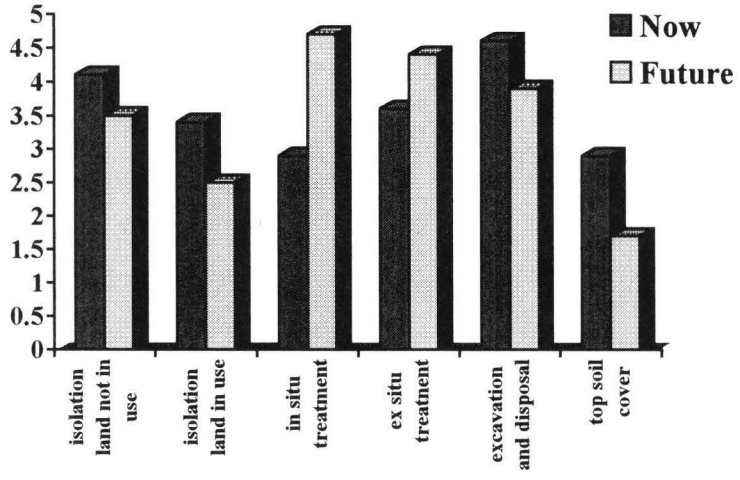


Figure 1: *Estimated use (ranging from 1 (less used) to 6 (most used)) of remedial options now and and in the future (next 5 - 10 years). The chart is based on the averaged value of the numerical ranked responses.*

The most commonly used methods at present are the conventionally engineered approaches including site containment and excavation and off-site disposal. The use of cover systems to protect on-site users from undisturbed contamination is also common to many countries. In the next 5-10 years most countries expect the pattern of use to change. The most anticipated changes are a reduction in the use of site containment and cover systems. In parallel, an increased use of the newer treatment methods especcially *in situ* techniques is reported. Many countries expect that excavation and disposal will remain a significant option for site management in future, depending on the legislative frameworks in individual countries.

Conclusions

Initial results and analysis indicate that the data are providing extremely useful and unique information which can be used to the benefit of all countries in the Group. In addition, a first comparison of the results of the Amsterdam Questionnaire with the Vienna Questionnaire results indicates a clear process of policy development in various countries: countries are moving towards more integrated solutions for contaminated land problems, seeking to combine environmental, socio-economic and planning approaches, all in cooperation with the market.

References

1. Visser, W.J.F., 1996. Analysis of the Vienna Questionnaire. UK Department of the Environment.
2. Visser, W.J.F., Elkenbracht, E.M., Johnson, S.T., Martin I.D. and Bardos, R.P., 1997. Analysis of the Amsterdam Questionnaire. Preliminary report. Dutch Ministry of Housing, Spatial Planning and Environment, Department of Soil Protection, (Final report to be published in Spring 1998).

THE AD HOC INTERNATIONAL WORKING GROUP ON CONTAMINATED LAND

Authors: W.J.F. Visser[1], I.M. Skovgaard[2] and C. Hoppener[3]
[1] Tauw Milieu, P.O. Box 133, 7400 AC Deventer, The Netherlands
[2] Danish Environmental Protection Agency, Strandgade 29, DK-1401 Copenhagen-K
[3] Dutch Ministry of Housing, Spatial Planning and Environment, Soil Department, Code 625, P.O.Box 30945, 2500 GX The Hague, The Netherlands

This poster was prepared on behalf of the *Ad Hoc* International Working Group

Keywords: contaminated sites, international cooperation, policies, risk management, groundwater protection, soil protection, soil remediation, sustainable soil use.

Nature and scope

The *Ad Hoc* International Working Group on Contaminated Land is an informal forum for international cooperation and exchange. The principal purpose of the Group is:
'to provide a forum, open to any country, in which issues and problems of contaminated land and groundwater can be discussed at a national level and information freely exchanged to the benefit of all participants'.
The Group's strength and value therefore relies on the national membership of countries or politically separate regions. Attendees are usually either from government environmental departments or environmental agencies or represent international organisations.

A brief history

The *Ad Hoc* International Working Group was formalised and had its first meeting in Vienna, Austria in November 1993, which was attended by representatives of government and government environmental agencies from 18 countries and a number of international organisations. Austria and the United Kingdom chaired the meeting.
A further two meetings were subsequently held, in Nottingham, UK (1995), jointly chaired by the United Kingdom and the Netherlands, and in Amsterdam (1997), with the Netherlands and Denmark providing the chairs. New countries were taken on board and by 1997, about 30 countries and international organisations participate in the Group, with the countries representing all continents and reflecting all stages of policy development and implementation.

Results: worldwide interaction and networking

The Vienna meeting demonstrated that countries share many common issues in developing and implementing policy approaches on contaminated land and groundwater. Countries welcomed the idea of (further) international collaboration and exchange. At the Nottingham meeting it was recognised that there is an increasing convergence in policy approaches, both regarding strategic objectives of contaminated land policies, and at the operational level, for instance referring to the technical principles behind risk assessment and risk management. In addition, arrangements were made to set up informal international working groups to study specific subjects in between meetings. These include:

- Third party financing;
- Registration of contaminated sites;
- Risk management approaches;
- Technology choices.

At the Amsterdam meeting, results of these informal working groups were reported and arrangements were made to further develop these discussions.

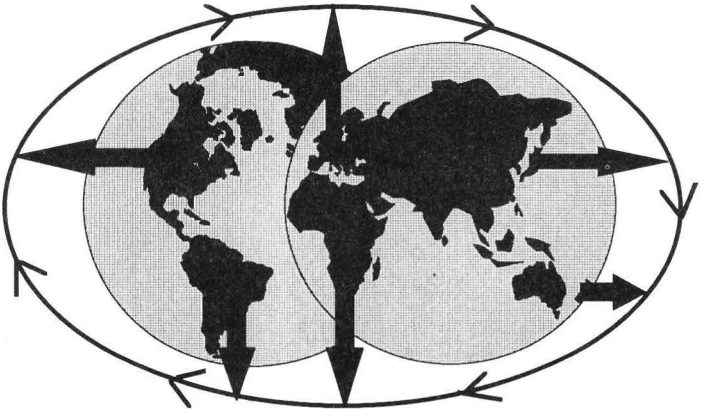


Figure 1: Ad Hoc International Working Group: Worldwide Interaction

Outputs

Results of the meetings are summarised in reports. Apart form the meetings the initiative was taken to produce a questionnaire to be circulated among the members of the Group *(see accompanying poster)*. Since 1996, a newsletter is being produced.

Conclusions

The *Ad Hoc* Group consists of a worldwide network of countries, represented by national or regional governments. The network provides opportunities for informal and formal cooperation and information exchange on contaminated land policies and implementation of these policies. This cooperation is essential because many countries share the experience that the problem of contaminated land is much more complex and has a much larger scale than first assumed.

Over the four years the *Ad Hoc* Group has been in existence, cooperation between Group members and the resulting exchange of experiences and information has contributed to a better state of knowledge, both at national and international levels. Countries are aware that solutions for contaminated land problems need to have a long term perspective, integrating environmental, economic and social interests.

The *Ad Hoc* Group is part of and provides links to a broader international network.

References

1. *Ad Hoc* Group, 1993. Report of Meeting in Vienna, Nov. 1993. UK Department of the Environment.
2. *Ad Hoc* Group, 1995. Report of Meeting at the Nottingham Trent University, UK, 16-17 May 1995. Dutch Ministry of Housing, Spatial Planning and Environment, Department of Soil Protection.
3. *Ad Hoc* International Working Group on Contaminated Land, 1998. Report of Meeting in Amsterdam, 29-30 May 1997. Danish Environmental Protection Agency.

International Networks on Contaminated Land - An Overview

H. Kasamas[1], J. Denner[2], I-M. Skovgard[3], and P. Bardos[4]

[1] CARACAS Office, Breitenfurterstr. 97, A-1120 Vienna, AUSTRIA
[2] Environment Agency, Steel House, Tothill Street, London SW1H 9NF, UK
[3] Danish EPA, 29 Strandgade, DK-1401 Copenhagen K, DENMARK
[4] R[3] Environmental Technology Ltd, PO Box 58, Ware SG12 9UJ, UK

Key Words: authorities, contaminated sites, knowledge transfer

SUMMARY
Some international initiatives concerning various aspects of contaminated land have been launched in the last years. Their overall intention is to avoid parallel efforts in the improvement of scientific and technological development and to exchange experience in the management of contaminated land related problems. This paper aims to provide an overview about currently on-going international initiatives on contaminated land, and introduces their objectives and actual results.

KURZFASSUNG
In den letzten Jahren wurden mehrere internationale Initiativen zu altlastenrelevanten Themen ins Leben gerufen. Das Ziel dieser internationalen Zusammenarbeit ist eine koordinierte Vorgangsweise, um paralleler Anstrengungen bei der technischen und wissenschaftlichen Entwicklung von Technologien zu vermeiden, und die Bereitschaft zum Erfahrungsaustausch über die in den einzelnen Ländern unterschiedliche gehandhabten Bewältigung der vielfältigen Probleme. Dieser Beitrag gibt einen Überblick über derzeit laufende internationale Initiativen und beschreibt deren Ziele und Ergebnisse.

INTRODUCTION

Some international initiatives concerning various aspects of contaminated land have been launched in the last years. Their overall intention is to avoid parallel efforts in the improvement of scientific and technological development and to exchange experience in the management of contaminated land related problems. This paper provides an overview about some currently on-going international initiatives on contaminated land, and introduces their objectives and actual results.

NATO/CCMS PILOTSTUDIES

NATO established the Committee on the Challenges of Modern Society (CCMS) in 1969. A fundamental precept of CCMS involves the transfer of technological and scientific solutions among nations with similar environmental challenges. The following Pilot Studies have been launched to cover contaminated site related problems:

NATO/CCMS Pilotstudy "Evaluation of Demonstrated and Emerging Technologies for the Treatment and Clean-up of Contaminated Land and Groundwater"

Background

The Pilot Study on treatment technologies for contaminated land and groundwater was initiated in 1986. Since then, the Pilot Study conducted two Phases. Phase I was completed in 1991, Phase II in 1997. A new Phase III has been started resently and will end in 2003. The Pilotstudy is chaired by the United States and co-chaired by Germany and the Netherlands. The Pilot Study organises annual technical conference for official participants from 17 countries.

Objectives

The Pilot Study is designed to identify and evaluate innovative, emerging and alternative remediation technologies and to transfer technical performance and economic information on them to decision makers and potential users.

Results

Proceedings of the technical conferences are published each year and are available from country representatives. Final Reports are published at the end of each Pilot Study phase, summarising the conclusions drawn during the respective Pilot Study period.

Additional information

Available from the US-EPA Homepage at *http://clu-in.com/intup.htm#International*. This Pilot Study will be also presented at ConSoil '98 (Theme A.1-Lecture Session: International Co-operation)

NATO/CCMS Pilotstudy "Environmental Aspects of Reusing Former Military Lands"

Background

This Pilot Study has been established to face the challenge of reusing former military bases. Workshop meetings are organised including participants from NATO- and for-

mer Eastern European countries. The Pilotstudy is co-chaired by the United States and Germany.

Objectives
Co-operation between NATO and former Eastern Bloc Countries countries in defining clean-up strategies for contaminated military properties.

Results
5 working groups have been established 1./ to set-up a uniform reporting format, 2./ to identify appropriate clean-up technologies and select demonstration sites, 3./ to establish a suitable format for data and information management, 4./ to evaluate economic, political and social aspect in the participating countries with regard to contaminated military sites, 5./ to identify potential national and multinational funds to carry out demonstration projects on selected sites.

Additional information
The Pilot Study will be presented at ConSoil '98 (Theme A.1-Lecture Session: International Co-operation)

AD HOC INTERNAT. WORKING GROUP FOR CONTAMINATED LAND

Background
The Ad Hoc International Working Group was initiated in 1993. Participants are representatives from environmental ministries and agencies. The Ad Hoc International Working Group involves 20 different countries world-wide and international organisations such as FAO and OECD. The Ad Hoc Working Group covers aspects of contaminated land policies, particularly legislative and administrative approaches.

Objectives
The main purpose of the Ad Hoc International Working Group is *to provide a Forum, open to any country, in which the issue and problems of contaminated land and groundwater can be discussed at a national level and information can be freely exchanged* to the benefit of all participants.

Results
All participating countries provided detailed information on various issues concerning their national approaches on contaminated land (Vienna Questionnaire 1994, Amsterdam Questionnaire 1996). These questionnaires include information on policy, liability, funding, assessment, prioritisation, and remedial treatment aspects. The reported data was analysed and published by the UK, Department of the Environment (1996) and the Dutch VROM (1997). These surveys aims to evaluate the state-of-the-art of contaminated land policies and approaches world-wide and to predict future developments.

The Ad Hoc International Working Group will be presented at a ConSoil '98 (Theme A.1-Poster Session: International Co-operation)

COMMON FORUM FOR CONTAMINATED LAND IN THE EUROPEAN UNION

Background

The Common Forum is a platform of co-operation between representatives of the EU member states, the European Commission, and the European Agency on issues related to contaminated land in Europe.

Objectives

The Common Forum serves as a platform 1./ to identify thematic areas for EU-wide co-operation, 2./ to enhance the dialogue between the different international activities, 3./ to collect and discuss the results of these activities and to make recommendations on technical issues and practical aspects to the European Commission and the European Environmental Agency, 4./ to facilitate the understanding of each EU Member State's approach to tackling the problem of contaminated land.

Results

At its first meeting in Bonn 1994, the Common Forum recommended to initiate an EU-wide project on risk assessment for contaminated sites. This led to the initiation of the Concerted Action CARACAS (see below). Due to the fruitful co-operation established with CARACAS, the Common Forum agreed to initiate another joint project to elaborate recommendations for sound management of contaminated sites in the EU Member States (CLARINET).

CARACAS - CONCERTED ACTION FOR CONTAMINATED SITES IN THE EUROPEAN UNION

Background

CARACAS is a Concerted Action initiative within the Environment and Climate Programme of the European Commission DG XII. 16 European Countries are represented in CARACAS with their environmental authorities and scientific advisors. CARACAS started in 1996.

Objectives

The main objective of CARACAS is to co-ordinate current research initiatives on contaminated land risk assessment carried out by the European Member States. Furthermore, CARACAS defines and recommends priority research tasks for future R&D programmes to improve current scientific knowledge in an co-ordinated manner throughout Europe.

Results

The CARACAS R&D Database includes information about more than 600 on-going R&D Projects on Contaminated Land Risk Assessment. The practical State-of-the-art on risk assessment in Europe has been evaluated and summarised with a CARACAS publication. The assessment includes up-dated information on national risk assessment methodologies and current research activities in the European member states. Additionally, priority research needs on contaminated sites risk assessment have been identified and recommended for inclusion to various R&D programmes in Europe.

Additional information
Can be obtained from the CARACAS Web Site at *http://www.caracas.at*. CARACAS will be presented at ConSoil '98 by oral presentation and poster (Theme A.1-Lecture Session and Poster Session: International Co-operation). CARACAS results will be discussed in a workshop session (A.2-Workshop: International networks/Concerted Actions on Contaminated Sites in the EU)

NICOLE - NETWORK FOR INDUSTRIALLY CONTAMINATED LAND IN EUROPE

Background
NICOLE is a Concerted Action of the Environment & Climate Programme. It has been created to bring together problem holders and researchers throughout Europe. NICOLE is industry-led and started in 1996. Industrial and scientific parties can obtain membership for the NICOLE network.

Objectives
NICOLE provides a European forum for the dissemination and exchange of scientific and technical knowledge and ideas relating to all aspects of contaminated land arising from industrial activities. It aims to promote co-ordinated, multidisciplinary collaborative research that will enable European industry to efficiently and cost-effectively identify, assess and manage contaminated sites.

Results
NICOLE has organised various workshops and conferences on specific aspects of contaminated site management. NICOLE's newsletter and Web Site provide actual information on all relevant issues concerning contaminated land. Priority research needs have been identified and recommended for inclusion in future R&D programmes.

Additional information
Available from the NICOLE Web Site at *http://www.nicole.org*. NICOLE will be presented at ConSoil '98 by oral presentation (Theme B.2 - Lecture Session: Industrial). NICOLE results will be discussed in a workshop session (A.2-Workshop: International networks/Concerted Actions on Contaminated Sites in the EU)

CLARINET - CONTAMINATED LAND REHABILITATION NETWORK FOR ENVIRONMENTAL TECHNOLOGIES

Background
CLARINET is a Concerted Action initiative within the Environment and Climate Programme of the European Commission DG XII. 16 European Countries are represented in CLARINET with their environmental authorities and scientific advisors. CLARINET will be launched in mid 1998.

Objectives
The primary objective of CLARINET is the development of technical recommendations for sound decision making for the rehabilitation of contaminated sites. CLARINET will provide a multidisciplinary scientific platform, integrating environmental,

technical, societal and economic aspects. It will provide a network for scientists, authorities, and problem holders. It aims to link various international activities on contaminated land.

The scope of CLARINET will be discussed in a workshop session (A.2-Workshop: International networks/Concerted Actions on Contaminated Sites in the EU)

RACE - RISK ABATEMENT CENTER FOR CONTAMINATED SOIL IN THE CEE COUNTRIES

Background

RACE has been established by the Institute for Ecology of Industrial Areas in Katowice/Poland in 1996 in response to the need for comprehensive, cost effective, environmental risk assessment and reduction strategies in the Central and Eastern European Countries (CEE).

Objectives

The major task is to facilitate co-operation in the field of risk abatement in CEE countries. RACE provides a forum for implementing significant policy changes, technology transfer, and increasing public awareness in CEE countries. It aims to contribute to the development of risk-based standards for soil and groundwater clean up in CEE countries, which will be acceptable for EU.

Results

RACE has organised various workshops for decision makers and researchers in CEE countries. The RACE newsletter provides information for CEE participants.

EUROPEAN TOPIC CENTER ON SOIL (ETC/S)

Background

The European Environment Agency (EEA) was established to collect, generate and provide objective, reliable and comparable information and data on environmental issues in Europe. A number of European Topic Centers have been established by EEA in this regard. One of them, the European Topic Centre on Soil (ETC/S) started its work in 1996.

Objectives

The objective of the ETC/S is to provide and develop information and data about soil conditions and status in all European countries. This includes data concerning contaminated sites. The ETC/S aims to propose a common framework on national inventories in order to provide the EEA with comparable and reliable information for estimating the problem posed by contaminated sites in Europe.

Results

Data on the Management of Contaminated Sites in the EU and EFTA States have been collected, reviewed and compared. Currently applied methodologies on contaminated site identification and their comparability have been examined.

ISO TC 190/SC 7 Soil Quality - Soil and Site Assessment

Background

ISO is a world-wide federation of national standardisation bodies, ISO TC 190 deals with the standardisation of soil quality, including classification, definitions, sampling, analysis and reporting of soil characteristics. The subcommittee SC 7 within TC 190 was established in 1995.

Objectives

The scope of ISO TC 190/SC 7 is to prepare international standards for the reuse of soil material, for assessment of possible groundwater impact due to contaminated soil, ecotoxicological aspects of soil investigations and possible effects caused by human exposure to contaminated soils considering various exposure pathways.

Results

Following documents are in preparation within ISO TC 190/SC 7:

- Requirements for characterisation of excavated soil and soil materials for re-use
- Soil relating to groundwater impact
- Guidance on the ecotoxicological characterisation of soils and soil materials

The ISO TC 190/SC 7 will be presented at a ConSoil '98 (Theme B.3 Workshop-Standards & Protocols)

References

CARACAS (1997), *Basic Information Report*, CARACAS

CARACAS (in press) *State-of-the-Art on Contaminated Land Risk Assessment in Europe*, CARACAS

Danish EPA, VROM (1997) *Ad Hoc International Working Group on Contaminated Land, Position Paper*, pp. 1-6, Danish Environmental Protection Agency, Denmark

German Environmental Agency (1997) *International Experience and Expertise in Registration, Investigation, Assessment, and Clean-Up of Contaminated Military Sites*, TEXTE 5/97, Environmental Agency, Germany

Leenars, H., Okx, J.P. (1997) *NICOLE Opinion on Contaminated Land Research in the Fifth Framework Programme*, NICOLE

Martin, I., Bardos, P. (1995) *A Review of Full Scale Innovative Treatment Technologies for the Remediation of Contaminated Soil*, Royal Commission on Environmental Pollution, United Kingdom

Olfenbuttel, R.F. et al (1993) *Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater, Final Report Phase I*, 3 Volumes, North Atlantic Treaty Organisation's Committee on the Challenges of Modern Society

Risk Abatement Center for Central and Eastern Europe (1996) *RACE NEWS, No. 1,* Institute for Ecology of Industrial Areas, Poland

Skovgaard, I.M., Strobaek, N. (1996) *Ad Hoc News*, No. 1/1996, pp. 1-4, Danish Environmental Protection Agency, Denmark

Smith, M.A. et al. (in press) *Evaluation of Demonstrated and Emerging Technologies for Treatment and Clean-Up of Contaminated Land and Groundwater, Final Report Phase II*, North Atlantic Treaty Organisation's Committee on the Challenges of Modern Society

Ulrici, W. (1995) Internationale Erfahrungen zur Altlastensanierung, Environmental Agency, Germany

Vegter, J., Ferguson, C. (1998) *Research and Development Needs for the Improvement of Contaminated Land Risk Assessment*, CARACAS

Visser, W.J.F. (1994) *Contaminated Land Policies in some Industrialized Countries*, Technical Soil Protection Committee, The Netherlands

Visser, W.J.F. (1996) *Analysis of the Vienna Questionnaire*, UK Department of the Environment, United Kingdom

Visser, W.J.F., Martin, I. (1997) *Results of the Amsterdam Questionnaire*, Dutch Ministry of Housing, Spatial Planning and the Environment, The Netherlands

Theme B:
Policies and strategies, governmental and industrial standards and protocols

The French National Approach to a simplified risk assessment

D. Darmendrail [1], B. Sauvalle 2
[1] BRGM - CT DEFIS, Fort de Lezennes, 59260 Lezennes, France
[2] Ministère de l'Aménagement du Territoire et de l'Environnement, 20 avenue de Ségur, 75302 Paris 07 SP

Keywords : Environmental policy instruments, risk assessment, classification, industrial sites, contaminated sites.

Introduction

The French national policy on management and remediation of contaminated sites, defined in a Ministerial directive dates December 3, 1993, can be summarized as follows : Inventory, Selection, Treatment. The selection system functions as a 4-stages screening set, based on assessment of risks generated for public health and the environment. Each screen relates to a diagnosis level requiring further and finer investigations. The second step involves an initial diagnosis (so called 'soil study') and a simplified risk assessment.

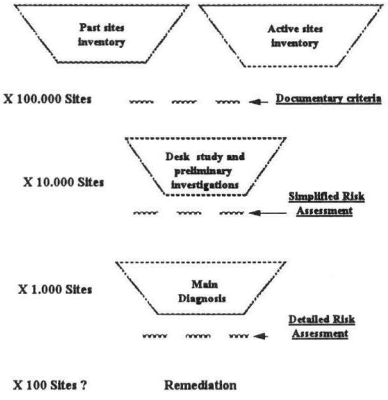


Figure 1 - French selection system

Principles of the Simplified risk assessment

The aims of the Simplified Risk Assessment (SRA) are :

- to distinguish sites that do not present danger for human health and the environment (in particular sensitive use of waters as drinking water) from those that may cause substantial and long-lasting harmful effects;
- to prepare items useful for decision-making purposes; sites are ranked in three categories as a function of actions to be carried out vs declared uses, either current or future (sites requiring further investigation and detailed risk assessment -classe 1, site to monitor requiring definition and installation of survey devices and possibly measures related to the control of urban planning - classe 2, 'commonplace' sites that may be considered compatible with a given use - classe 3).

The SRA is based on a scoring method using technical paramaters following the principle of risk assessment : the existence of a risk implies the presence of a dangerous source (D), mode(s) of transfer toward and into media (Tr), and existing targets (T). Technical criteria have been defined for each of the factors (D,Tr, T), enabling them to be characterised (on the basis of informations obtained during the initial diagnosis). 49 parameters have been chosen for the SRA, distributed in four items : 'potential danger of the source', 'potential for mobilisation and transfer of polluting substances', 'target' and 'observed impact'.

Each criterion is scored as a function of the values that they may reach. The basic scores are then combined in order to provide overall scores that correspond to the different exposure routes identified for the studied sites. Nine scoring grids have been defined : three for groundwater (drinking water supplys, others uses, future resource), three for superficial waters (same uses), one for soil by direct contact, one for air by direct contact and one for risks of fire/explosion. In practice and depending on the context of the site (presented in a conceptual model), only the scoring grids that are relevant for the source or the site should be retained.

Results of the national test

The first version of the SRA has been tested on 200 industrial sites (either active or former sites, potentially or known contaminated sites, covering all types of industrial activities - chemistry, gasworks, smelters, ...). The main recommandations are :

- the SRA must be a real joint operation among the different participants (site manager, consultants, administration) in order to be effective;
- Reliability and precision of the available data for scoring is now taken into account. If the information is insufficient for attributing an overall score, initial investigations must be extended;
- The development of French guidelines values for soils is necessary to score the level of the observed impact vs several uses (residential with ou without vegetables, industrial, office uses). Provisional guidelines values have been defined based on foreign practice, in order to start the regulatory studies on about 1.580 sites;
- These modalities are still considered as provisional. These modalities will be reexamined and modified if necessary with 'feedback' from the application of the SRA to a larger number and greater diversity of sites.

References

Ministère de l'Aménagement du Territoire et de l'Environnement (1997) *Gestion des sites (potentiellement) pollués, version 1, juin 1997,* Editions du BRGM.

Darmendrail D. (1997) Technical guidance documents for the French policy for Treatment and rehabilitation of polluted sites; Porgress as of 01/09/1996, in CARACAS basic information report, Vienna (Austria).

RELEASE OF THE NETHERLANDS GUIDELINE ON SOIL PROTECTION AT INDUSTRIAL SITES (NRB)

P.A. Ruardi and O.Z. van Sandick

Ministry of Housing, Spatial Planning and the Environment
Soil Department IPC 625, P.O. Box 30945, 2500 GX The Hague,
The Netherlands

Theme B

Key words: Governmental directives,impermeable industrial flooring, industrial sites, knowledge transfer, monitoring procedures, prevention, quality assurance, risk analysis, soil protection policy, soil protection technology.

SUMMARY
The - Netherlands Guideline on Soil Protection at Industrial Sites (NRB) - informs about preventive provisions and measures for industrial activities and facilities. It describes the state of the art of soil protection technology and incorporates a decision support system for the choice of the adequate protection strategy.

KURZFASSUNG
Die - Niederländische Richtlinie Bodenschutz gewerbliche Aktivitäten - informiert über präventive Vorkehrungen und Massnahmen für gewerbliche Aktivitäten auf Industrieflächen. Sie beschreibt den Stand der Technik von Bodenschutztechniken und enthält eine Entscheidungsmethodik zur Wahl der geeigneten Schutzstrategie.

RÉSUMÉ
La - Directive Néerlandaise Protection du Sol au terrains industrielles - informe des mesures préventives pour des activités d'exploitation au terrains industrielles. La directive décrie les techniques de protection du sol préventive et contienne une methode de décision pour choisir le strategie de protection adéquate.

Contaminated Soil '98, Thomas Telford, London, 1998, 745–747

The Netherlands Guideline on Soil Protecton at Industrial Sites (NRB) (ref. 1 and 2), released end of 1997 / early 1998, focusses on preventive soil protection provisions and measures for industrial activities and facilities. It is a manual to define an optimal choice for soil protection, based on the described state of the art of science and technology. The NRB is formulated by close co-operation between representatives of authorities, industry and engineering companies.
Local authorities use the NRB for writing environmental permits. A permit is founded on the involved company's requisition with information based on the NRB.
In 1998/1999 the NRB will be adapted after evaluation based on gained experience.
The NRB has been notified by the EC in Brussels.
The Netherlands implemention program for the preventive soil protection policy was mentioned in a paper on the TNO-KFK congres Contaminated Soil '93 in Berlin (ref 3).
Soil protection measures for localized sources of potential soil contamination distinguishes between emission preventing (installation or equipment orientated) measures and containment (isolative) measures. Environmental policy concentrates on emission prevention but when this is not possible or feasible, isolative measures will be necessary for soil protection. Proces -, installation -, or equipment related means and measures are not included in the NRB. Those measures are pursued within the more integral environmental and safety policies.
The measures described in the NRB are based on the ALARA-policy (emissions as low as reasonably achievable), stated in the Netherlands Environmental Law. The NRB concerns both existing and new activities.
The NRB facilitates the implementation of the national environmental policy and legislation about soil protection by description of the state of the art of technology, risk analysis, environmental care and quality assessment.
The NRB incorporates:
* the national policy and regulations on soil protection at industrial activities.
* the state of the art of technology, with respect to impermeable flooring, pavements and liners at soil endangering facilities/activities, drainage systems/sewerage, large storage tanks and monitoring (systems) of soil quality.
* a decision support system for soil protection strategy, based on soil risk approach and protection efficiency.

The most important project concerning the NRB is the Project on Soil Protection Provisons (PBV), organised and partly financed by the civil engineering industry. The PBV started in 1993 and provides:

- o rules for design and calculation
- o recommendations for construction
- o procedures for construction and
- o quality assessment via certification.

The PBV stretches beyond the NRB and comprises not only soil protection at industrial facilities but also at agricultural facilities, garages, petrol stations, application of residues in constructions and (waste) landfills. The major part of PBV is knowledge description allthough some knowledge development, especially on permeability of materials is incorporated.
The PBV guides the design, the realisation and the use of adequate and reliable protective constructions. For isolative constructions of assured quality a structure of documents is needed that translate the environmental regulations in

concrete requirements.
Three organizations are responsable for the project:
CUR: Research and Regulation of civil engineering and construction;
NIBV: Information and knowledge transfer on protective constructions;
KIWA: Quality assurance, certification and inspection.
These organisations co-operate in the PBV succesfully with the industry and the authorities on a public-private base.
The state of the art of protection technology has been developed already in such a way that important questions, such as about impermeablity of materials and constructions, can be answered correctly. The requirements for the realisation of protective constructions are being laid down in prenormative documents like PBV/CUR-Recommendations and Independent Evaluation Guidelines for product- and procescertification (BRL's).
A manual for the design of protective constructions, including construction details and an instruction book for a course on the application of the NRB will be made available.
The first phase of the PBV finishes end 1998 and will be continued with phase II from 1999 till 2004. At the end of phase II all the necessary knowledge for soil protection by isolative provisions and measures at industrial sites should have been developped, described and transfered to the target groups and the quality of protection assured.

Other NRB-related projects are:

- o the decision support system (what protection where), consisting of a sequence of prescribed steps to be followed by the user. It contains a Soil Protection Decision Model (BBB), comprising a soil emission risk analysis method (developed by TNO-MEP).
- o the Guideline on Soil Protection at Large Storage Tanks (flat bottom tanks), in co-operation with Europoort Belangen Botlek (EBB) and
- o the Guideline on Monitoring (procedures) of Soil Quality at Industrial Sites.

These guidelines are to be considered as basic documents for the NRB, to be used together with the NRB.
Special attention will be paid to the necessary knowledge transfer to the target groups of the NRB, via symposia, workshops and courses. The NRB will be adapted when development of the state of the art of science and technology makes that necessary.

This paper is linked to three other poster papers:
1. about the Soil Protection Decision Support System (BBB) and about a pc-operated automation system for the BBB 'ASSISTERIX' by De Weger (TNO-MEP).
2. about the Guideline on Monitoring (procedures) of Soil Quality at Industrial Sites by Van Vossen and Slenders (IWACO).

References:
1. Nederlandse Richtlijn Bodembescherming bedrijfsmatige activiteiten NRB (1997, 1998) InfoMil , Den Haag,
2. Netherlands Guideline on Soil Protection at Industrial Sites NRB (1998) VROM/NIBV, Woerden, concise english translation of ref. 1.
3. Ruardi P.A. (1993) Preventive soil protection at industrial sites in F. Arendt et al (eds) Contaminated Soil '93 Kluwer Academic Publishers, Dordrecht, pp 1529-1536.

IMPLEMENTATION OF TITLE IX OF THE EUROPEAN BASIC SAFETY STANDARDS DIRECTIVE CONCERNING INTERVENTIONS AS A RESULT OF RADIOACTIVE MINING RELICS INTO GERMAN LAW

K. Wichterey [1], S. Przyborowski [1] and Ch. Sangenstedt [2]

[1] Federal Office for Radiation Protection, Köpenicker Allee 120 - 130, D-10318 Berlin
[2] Federal Ministry for the Environment, Nature Conservation and Nuclear Safety, Schiffbauerdamm 15, D-10117 Berlin

Key words: regulations, national law, mining, radioactive contamination, remediation concept, exposure, reuse

Council Directive 96/29/EURATOM of 13 May 1996 laying down basic safety standards of the protection of the health of the workers and the general public against the dangers arising from ionizing radiation, hereinafter called the Directive, has to be implemented into national law within four years.

At the same time, there is an additional requirement in Germany to unify radiation protection law. As a result of German unification, there are different regulations in East and West Germany concerning exposure due to natural radiation sources. Especially for the clean-up of radioactive mining relics and former uranium mining and milling sites a common legal basis for both East and West Germany has not been established yet.

Title IX of the Directive applies to interventions in cases of lasting exposure resulting from the aftereffects of a past or old practice or work activity, even when caused by natural radiation. Radiation exposures resulting from mining relics (traditional ore mining as well as uranium mining) belong to situations of the intervention type because the problem has arisen at a time with no or insufficient radiological knowledge or regulation.

The implementation of the Directive concerning this situation and the solution for the special problem in Germany is discussed to be realized in the following way:

1. Amendment of the German Precautionary Radiological Protection Act.
2. Creation of a new ordinance concerning radiation protection at contaminated sites.

The aims of the new ordinance are supposed to be:

- guarantee of appropriate radiation protection
- high practicability considering administrative and economic circumstances.

The intention is to tackle the problem realistically but sufficient conservatively. Decision making in that field has to take into account, in which way the contaminated area should reasonably be re-used in the future. In that respect Germany does not follow multifunctional approach. A contaminated industrial area; for example, should primarily be recycled for industrial re-use. It does not necessarily have to be turned into an area suitable for dwellings.

Contaminated Soil '98, Thomas Telford, London, 1998, 749–750

This ordinance is oriented towards the draft of the German Federal Soil Protection Act which does not apply to radioactive contaminated sites.

A definition of the radioactive contaminated site should be given on the basis of a primary level of effective dose (in discussion: 1 mSv/a) which is valid in addition to the background. Below that level there should be no need for remedial actions (justification). Rehabilitation measures (including the possibility of restrictions) should only be required in bases of exceeded dose level. Methods of optimization should be applied for decision making and during the time of remedial actions.

Furthermore, the ordinance should contain derived levels for the specific activity of soil for unrestricted and restricted landuse. Relevant exposure pathways should be given with reference to calculation provisions of effective dose. Besides there should be regulations on responsibilities, costs, organization of regulative action and control, additional radiation protection measures for workers and the public etc.

"Hazards and protective measures associated with the handling of biological agents during soil remediation".

Ursula Schies,
Tiefbau-Berufsgenossenschaft, TAD, Landsberger Str. 309, D-80687 München, Germany

Key words: health and safety, microbiological soil remediation, occupational safety, prevention, regulation, risk assessment,

1. Introduction A great part of the contaminated soil is remediated by microbiological methods, adding culture solutions as well as externally cultivated microorganisms, if necessary. This gives rise to questions about work safety aspects of soil remediation measures, such as:

- Do these new methods also entail new "biological" hazards?
- Can microorganisms that degrade contaminants be pathogenic?
- Can biological hazards be expected only in the case of biological remediation?
- How should culture solutions and enrichment cultures be treated on the construction site?

In order to clarify these questions, general directions have been prepared under the responsibility of the Tiefbau-Berufsgenossenschaft, the statutory accident prevention and insurance institution for the civil engineering industry, entitled "The handling of biological working substances during soil remediation". These general directions simplify the task of ascertaining the hazards and assessing the risks involved in handling biological working substances during soil remediation. It also contains information about appropriate protective measures. The general directions thus take account of the requirements of EC Directive 90/679/EEC on the protection of workers against the hazards posed by biological working substances in the course of their work.

2. Risk assessment If there is no additional risk in comparison to normal handling of soil, the general protective measures are sufficient. In working ares with an additional biological risk, more extensive protective measures are inquired.The potential biological risk posed by a soil remediation measure depends on: the contaminated soil, the added biological agents and the remediation method.

2.1 Soil Most species of bacteria that were isolated and identified from water and soil samples are typical free circulating saprophytes, which break down dead organic substances, as well as organisms only becoming pathogenous under certain conditions and posing a low potential hazard for human beings. Human pathogenous microorganisms in Risk Group 3 are not usually encountered in the soil flora in Central Europe.

Human pathogenous microorganisms that could constitute a hazard to human beings can therefore only be expected in very rare exceptional cases, such as on former sites of

animal disposal plants or on sites used by the leather industry, for example tanneries. In these few isolated cases, it is advisable to test for anthrax bacteria (*Bacillus anthracis*) as a precaution. Appropriate protective measures must then also be coordinated with the representatives of the local health agents.

2.2 Biological Agents The biological agents involved in the remedial measures should be sub-divided into: nutrient solution, enrichment cultures and organic substrates.

In most cases *nutrient solutions* also contain easily utilisable C sources such as sugar, molasses, etc. Under non-sterile conditions saprophytes, for example Clostridia, can therefore probably multiply in the culture medium. Such nutrient solutions must therefore be used within 24 hours. If, however, they are kept for longer periods, for example operational reasons, they must be cooled. Otherwise, it can be assumed that pathogenous microorganisms have multiplied in the meantime, so that more comprehensive protective measures have to be taken.

With many remediation methods, microorganisms are added to the contaminated earth in the form of *pure cultures, enriched mixed cultures or "natural additives"*. Enrichment cultures should be hygienically safe. This is considered to be the case, when it can be guaranteed that only microorganisms from Risk Group 1 are used. In the case of mixed cultures, most of which also contain organisms from Risk Group 2, additional protective measures must be taken for the respective working stages.

If *organic substrates* are produced as carriers of immobilised microorganisms, the origin of the basic substances, such as fresh compost from composting plants, sewage sludge, liquid manure and other organic waste is essential for assessing the hygienic situation. The presence of pathogenous microorganisms must be expected here. In addition, it should be borne in mind here that it is mainly after the actual construction work, such as inspection or sampling of soil layers, that a hazard due to spores must be expected.

3. Safety measures In working areas, where there is no additional risk related to biological agents, the general work safety measures as discribed in the "Guidelines for working in contaminated areas" are sufficient. In working areas where more extensive protective measures are required, employees with skin injuries are as a rule not allowed to be occupied. Dependent on the kind of exposure, there are additional protectiv measures described in the supplement.

4. References

Directive 90/679/EEC "Council Directive on the protection of workers against hazards by biological agents in the course of their work" (7th Individual Directive in complicance with Article 16 Para.1 of Directive 89/391/EEC)

Anonymus. (1997) Regeln für Arbeits- und Gesundheitsschutz bei Arbeiten in kontaminierten Bereichen *Guidelines for working in contaminated areas* (ZH1/183). Tiefbau-Berufsgenossenschaft, München, Germany.

Anonymus (1996) Merkblatt über den Umgang mit biologischen Arbeitsstoffen bei der Bodensanierung *The handling of biological working substances during soil remediation* Tiefbau-Berufsgenossenschaft, München, Germany.

Criteria for selecting health risk levels to define soil clean-up objectives.

Pascal Empereur-Bissonnet [1], William Dab [1], Frédéric Dor [2]

[1] EDF-GDF, Service des Etudes Médicales, 22-30 avenue de Wagram 75008 Paris - France
[2] Agence de l'Environnement et de la Maîtrise de l'Energie, 27 rue L. Vicat 75015 Paris - France

Keywords: contaminated soil, human health risk, remediation, reuse (of sites), risk assessment, risk management, target values.

Since the early 1980s, management policies for chemically contaminated soils have been based primarily on public health criteria. The recent development of risk assessment procedure gives decision-makers access to quantified estimates of the health risks to present or future users of contaminated sites. The question that must next be answered is how to select the acceptable risk levels for human health on which clean-up soil values can be based.

The approach varies according to the nature of the toxic effects. Here we consider only the chronic hazards associated with human exposure to low doses of toxic substances, over long periods of time, as is the case when the assessment concerns the residential, recreational or commercial reuse of a site. The choice is easier when the effects occur above a particular dose limit: such a threshold mechanism applies to adverse effects that are not genotoxic. The usual objective in these cases is to protect the exposed population from all hazard, that is, to manage the site so that exposure never exceeds the toxicologic reference values; these are derived from no adverse effect levels (NOAEL) observed during human or animal studies. No such safety level is considered to exist for genotoxic-carcinogenic and mutagenic effects, and perhaps for some other non-carcinogenic hazards. Although the truth of this hypothesis remains the subject of serious scientific debate, it has been assumed as the basis for the precautionary principle of health risk management. Under the hypothesis of no-threshold effect, zero risk exists only for zero exposure, which, in practice, is nearly always impossible to obtain.

It is therefore necessary to define a tolerable level of cancer risk. There is not, however, any universal threshold level of risk that is societally acceptable. Defining this limit is vital since is becoming the principal basis of public decisions about human exposure, whether environmental or occupational. The question therefore deserves a wider discussion, at the highest parliamentary levels; such a debate would furnish the opportunity for a major educational effort to be directed at the public as well as its elected representatives. While we wait for this to come to pass, three criteria can be taken into consideration for defining the target values for soil clean-up.

1) The legal concept of "de minimis". It defines the risk levels that are below legislative or regulatory concern. Using this principle, some countries have arbitrarily chosen a lifetime risk limit for excess cancer of 10^{-6}. One-chance-in-a-million corresponds to a very low individual probability of developing cancer and it was originally intended to define a *negligible* and not an *acceptable* risk.

Applied to the management of contaminated soils, this limit of 10^{-6} seems excessively prudent. Remediation to reach this goal necessitates procedures that are both technically difficult and very expensive, for a marginal benefit to public health that is often very low. This attitude thus can rarely stand up to a cost-benefit analysis about the current issues in public health.

2) Background levels are a second possible criterion. A decision can be based on the supplemental risk added by the contamination specific to the site, assessed as a function of the local or regional background risk from soil and other media. The approach is interesting but would be difficult to implement in France, for example, where background levels are unknown for many regions and for a multitude of chemical substances of natural and especially human origin. Moreover, in zones where background levels alone entail a substantial risk, management would become quite difficult, even if the pollution were largely geochemical (high arsenic levels, for example).

3) The comparison of environmental risks and current management practices furnishes a third criterion. Environmental pollution, from natural (radon, arsenic) or anthropogenic (benzene, benzo[a]pyrène) sources, can produce an excess risk of cancer greater than 10^{-4} or 10^{-3}. Each of us is exposed, during our daily life activities, to risks of death or cancer in the range of 10^{-6} or 10^{-5} and even higher: eating barbecued food, breathing the air of our cities, living in an old or a new home, travelling by car, or smoking cigarettes. The levels set for environmental management are generally higher than 10^{-6}, as an examination of regulation in France and elsewhere shows. For example, WHO based its guidelines for drinking water on a lifetime excess risk of cancer of 10^{-5} (at least when this objective is reachable, which it is not for all pollutants), but the European Community public dose limits for ionising radiations correspond to a risk on the order of 10^{-4}. Occupational protection is based on acceptance of comparable or often higher levels of cancer risk: 10^{-3} for ionising radiations (Europe); 10^{-4} (Denmark), 10^{-3} (USA) and 10^{-2} (France) for benzene.

Overall, the comparative approach seems most consistent. It suggests that global human exposure levels, related to the use of a remediated site, should be based on an individual lifetime excess risk of cancer of 10^{-4} (that is, one supplemental case of cancer, associated with residual soil contamination, for the entire life of ten thousand exposed subjects). This level is already used by many decision-making bodies, for products that arouse substantial public agitation, including benzene and asbestos. This choice is further justified by the overestimation inherent in the risk assessment, which is based on multiple assumptions, all deliberately conservative. The risks to which users of a cleaned and reused site are really exposed are thus substantially overestimated. Whatever choice is made, a public debate is indispensable so that the difficult question of the risk level acceptable to society can receive a consensual response.

AN INTEGRATED REGULATORY APPROACH FOR RISK ASSESSMENT AND THE DEVELOPMENT AND USE OF GUIDELINE VALUES FOR CONTAMINATED LAND REMEDIATION IN THE UK.

R.C.Harris[1] and S.Herbert[2]

[1] Environment Agency, Olton Court, 10 Warwick Road, Solihull, W.Midlands, B92 7HX,
[2] Environment Agency, Steel House, 11 Tothill Street, London, SW1H 9NF, UK

Key words: Soil and groundwater contamination, risk assessment, target values, guidelines, software tool, regulations, remediation.

INTRODUCTION: Soil contamination can pose risks to a variety of classes of receptors:

- humans;
- the water environment;
- ecosystems and;
- building materials and engineering infrastructures.

The risks to any one receptor class must not be considered in isolation from others, either by a regulator or by those responsible for the site. The development of an integrated approach to the assessment of risks from contamination at any particular site is difficult since it requires decision-making to be based on often highly complex technical information. Balances have to be struck with limited resources between a number of equally demanding activities or goals. Nevertheless logical, transparent and defensible decision-making regarding the reduction of risks to acceptable levels, for the variety of receptors, is necessary.

RISK-BASED DECISION MAKING: In the UK regulatory setting, the Environment Agency (for England and Wales) is faced with the need to assess risks from soil contamination in a number of different contexts:

- The overall protection of the environment in determining activities/situations which present the greatest hazards and the areas which are most sensitive or vulnerable to pollution.
- The assessment of new development to determine the acceptability, constraints or engineering needs to mitigate potential impact.
- The regulation of existing operations or land/water quality to evaluate the activities/contaminants that pose the greatest threat and thereby prioritising regulatory actions.

Agency staff are drawn from many different disciplines but have traditionally been focused on discrete regulatory functions such as water quality and waste management regulation. Soil quality and contaminated land remediation are comparatively new areas of activity that require composite skills and multidisciplinary team working if an integrated approach is to be effective.

Although risk assessment is commonly used by both regulators and practitioners, and has been for some time, there has been little help in applying more advanced techniques in any

Contaminated Soil '98, Thomas Telford, London, 1998, 755–756

uniform or consistent way. Regulatory input can be at different levels, ranging from policy advice and guidance at the elementary level, through expert systems backed up with simple calculations, to sophisticated mathematical models. A range of tools and supporting guidance is therefore required to assist in making better informed decisions. Many tools are now becoming fairly readily available as this tiered approach finds international acceptance. However, there is a significant gap for devices which can be used with varying degrees of expertise to give a relatively cheap appraisal of potential impacts. Software packages are needed to fill the gap between expert systems and site specific models.

DEVELOPMENT OF ASSESSMENT TOOLS: Recent work, funded by the Department of the Environment, Transport and the Regions (DETR) and the Environment Agency, has focused on improving the range of tools available to regulators and the regulated, to assist in making better informed decisions and in achieving a more consistent approach. This work ranges from the development of procedural guidance for carrying out risk assessment through expert systems backed up with simple calculations, sophisticated mathematical models and the derivation of guideline or screening values. Emphasis is placed on tools which allow a flexibility of approach. This enables users to respond to site specific circumstances by firstly assessing the applicability of generic guideline values and then using more complex exposure and effects modelling to estimate risks, as appropriate. Generic values have to be conservative in order to cover most circumstances whilst the latter approach requires considerably more information and site investigation data. The site owner/developer therefore has to decide on the acceptance of remedial targets that may require the treatment or removal of larger volumes of soils and groundwaters, as opposed to investment in the procurement of more information that could lead to a lesser degree of remedial action, due to a more precise understanding of the risks.

Current UK good practice guideline values and tools available and, being developed, include:

- A model procedure for risk assessment (M.R Harris, A Model Risk Assessment Procedure for Contaminated Land (1998) 6th FZK/TNO Conference Consoil) ;
- CLEA model and guideline values for estimating chronic risks to human health;
- Methodologies for deriving remedial targets for polluted groundwater and soils to prevent on-going water pollution;
- ConSim model for estimating risks posed to the water environment by soil contamination (D.H.Hall et al, Quantifying the Risk Posed to Groundwater from Contaminated Land - the ConSim Model (1998) 6th FZK/TNO Conference Consoil);
- Tools for ecological risk assessment;
- Guidance for estimating risks to building materials.

Technical expertise is essential if risks from soil contamination are to be effectively and expeditiously assessed and the availability of tools such as guideline values is not intended to, and must not, reduce the need for expertise. (Educational programmes are also part of the Agency's work). Instead they are seen as important components of an overall package of guidance to assist regulators and practitioners in making defensible and consistent decisions efficiently.

A PRIORITY SYSTEM FOR THE RANKING OF CONTAMINATED SITES

J. Bronders (1), C. Cornelis (1), P. Geuzens (1), J. Nouwen (1) and J. Ceenaeme (2)

(1) Flemish Institute for Technological Research
Boeretang 200, B-2400 Mol, Belgium
(2) Public Waste Agency of Flanders
K. De Deckerstraat, B-2800 Mechelen, Belgium

Key words: classification, contaminated sites, priority lists, ranking system

1. Introduction

Under the Flemish Decree on Soil Remediation a distinction is made between historical soil pollution and new soil pollution (Van Dijck, 1995). Soil pollution is considered historical if it has been caused before the enforcement of the Decree. If the preliminary soil investigation (or exploratory investigation) on possibly contaminated sites, indicates the presence of pollutants, the need for further detailed soil investigation depends on comparison of the concentrations with soil cleanup values. During the detailed soil investigation (descriptive investigation) the pollution will be characterised in detail and the risk for humans and ecosystem will be defined. The need for remedial action is depending on the concentrations, the risks and the type of contamination (new or historical). In case of new pollution remedial actions are always needed when exceeding soil cleanup values. For historical pollution the risk for humans, animals, plants and ecosystem will determine if remedial action is necessary. The number of sites, where further investigation or remediation has to be carried out, is relatively high. Consequently, it is advisable to use a priority list. The Public Waste Agency of Flanders (OVAM), which is the Flemish authority competent for soil pollution and sanitation, has requested the Flemish Institute for Technological Research (VITO) to develop such a ranking system. With this ranking system OVAM is able to use objective technical and scientific arguments in support of their decisions.

2. Ranking system for sites where the exploratory investigation has been carried out

The sites considered in the ranking system are those where the historical pollution has been defined as a possible serious threat to humans and/or ecosystems. The following criteria are used in the ranking methodology: concentrations of pollutants in soil and groundwater; vulnerability of groundwater to pollution; use of the site (industrial, agricultural,...) itself and of the surrounding area; presence of and distance to surface water; estimated area of the polluted part of the site, and the presence of floating or sinking layers. A distinction is made between criteria related to the pollution itself (concentrations, vulnerability and use of the site) and the site characteristics (surface water, area, use of surrounding areas, and presence of free product). A global score (defining the final classification) is calculated using the following equation:

$$GS = [CI_{(SAP)} + CI_{(NSAP)}] * [m_1 + m_2 + m_3 + m_4] \qquad (1)$$

where: $CI_{(SAP)}$ and $CI_{(NSAP)}$ = concentration index for soil and groundwater ($CI_{(SAP)}$ for parameters belonging to the standard analytical package (SAP) and $CI_{(NSAP)}$ for other parameters analysed); m_1 = index depending on use of neighbouring areas (value from 0.1 to 1); m_2 = index representing presence of surface water (value from 0.1 to 0.3); m_3 = index depending on the estimated area where pollution is present (value from 0.5 to 1); m_4 = index equals 1 if free product is present otherwise equal to 0.

Contaminated Soil '98, Thomas Telford, London, 1998, 757–758

The concentration indices $CI_{(SAP)}$ or $CI_{(NSAP)}$ are equal to the sum of the concentration indices for soil and groundwater which are calculated as follows:

$$\mathbf{CI_{soil}} = \sum_{i=1}^{n} \frac{C_{ib}}{(BSN_{ib})^{(*)}} \quad \text{and} \quad \mathbf{CI_{groundwater}} = \sum_{i=1}^{n} \frac{C_{igw}}{(BSN_{igw})^{(*)}} \qquad (2)$$

where: CI = concentration index for soil and groundwater; C_{ib} and C_{igw} = highest observed concentration of parameter i in soil and groundwater (only concentrations higher than 0.8 times the cleanup values are considered); $BSN_{ib}^{(*)}$ = cleanup value for parameter i in the soil; $BSN_{igw}^{(*)}$ = cleanup value for parameter i in groundwater.

3. Ranking system for sites where the descriptive investigation has been carried out

The sites where the descriptive investigation has shown the presence of serious threat to humans and/or ecosystem are classified using another methodology. A global score, GC, is defined as:

$$\mathbf{GC = Cf * Vf * Bf} \qquad (3)$$

The weights Cf, Vf and Bf are defined as follows: Cf is the extent and the concentration of the pollution; Vf consists of the site characteristics defining the spreading of the pollution; Bf is the human exposure. These weights are defined as given below.

$$\mathbf{Cf = [(CI_{soil(SAP)}+CI_{soil(NSAP)})*m_3] + [(CI_{grw(SAP)}+CI_{grw(NSAP)})*m_5]+m_4} \qquad (4)$$

where: CI = concentration index for soil and groundwater (see eq. 1 and 2). In this case the average concentration of the considered parameter is used. Concentrations higher than 0.8 times the cleanup values are taken into account; m_3 and m_5 are depending on the volumes of contaminated soil and groundwater and varies between 1 and 5; m_4 is the area (m^2) where free product is present.

$$\mathbf{Vf = [m_1 + m_2 + m_6] + [(m_7+m_8+m_9) / m_{10}]} \qquad (5)$$

where: m_1 and m_2 as defined in equation 1; m_6 is a coefficient depending on the distribution coefficient and varies between 0 and 1; m_7 = drainage factor (for drainage m_7 = 0, for recharge m_7 = 1); m_8 = groundwater flow coefficient depending on the flow velocity and varying between 0 and 1; m_9 = coefficient defining the flow time towards a receptor, varying between 0.25 and 1; m_{10} = coefficient defining the quality of the deeper groundwater, varying between 0.25 and 1.

$$\mathbf{Bf = m_{11}} \qquad (6)$$

where: m_{11} = coefficient defined by the results of a model where an estimation of the human exposure is made. m_{11} is defined as the summation of (DI_i / TDI_i). Where the DI_i is the calculated daily intake of pollutant i and TDI_i is the tolerated daily intake for the pollutant i.

4. References

Van Dijck E. (1995) The contaminated sites policy in Flanders Belgium. Contaminated Soil '95, Proceedings of the Fifth International FZK/TNO Conference on Contaminated Soil, 30 October - 3 November 1995, Maastricht, The Netherlands, pp. 39 - 48.

DEVELOPMENT OF CLEAN-UP VALUES FOR SOIL POLLUTION IN NATURE RESERVES

M.P. Goyvaerts and C. Cornelis

VITO (Flemish Institute for Technological Research), Boeretang 200, B-2400 Mol, Belgium

Key words : bioassays, computer model, contaminated soil, databases, ecotoxicological, heavy metals, intervention values for soil clean-up

INTRODUCTION

Clean-up soil standards for new soil pollution (pollution who took place after 28 October 1995) were implemented on the 29 of April 1995 (Vlaamse Gemeenschap 1995). The clean-up soil standards are differentiated in five land-use categories: nature, agriculture, residential, recreation and industry. The clean-up standards for the last four categories were obtained by the application of an exposure model using almost only human toxicological data. Some corrections were added based on phytotoxicity data and toxicity data for cattle. For the land-use nature ecotoxicological data are used. In wildlife areas, the ecological value need to be protected where for the other four land-uses men is the principal source of wariness.

The calculation of the proposed clean-up soil standards for the land-use nature are based on the approach posed by the Canadian Council of Ministers of the Environment (CCME, 1996). For application to the Flemish situation, slight modifications were made (Goyvaerts M.P., Cornelis C., 1996, 1997). One modification is the transformation of the ecotoxicological data to a standard soil with fixed amount of clay (10 %) and organic matter (2 %). The transformation formulas used are described in Vlarebo (Flemish Regulation on Soil Remediation). Secondly, all the ecotoxicological data related to soil microorganisms are used without making a hierarchical difference in the endpoints.

A preview exercise was done with ecotoxicological data gathered in the Netherlands by the RIVM (Denneman C.A.J., van Gestel C.A.M., 1990). Due to a lack of data for some heavy metals and the size of the databank, an enlargement with recent literature data was indispensable. A thorough literature study was done. Recently the databank was extended with data compiled by the Oak Ridge National Laboratory (ORNL, 1995a, 1995b).

APPLIED METHODOLOGY

The calculation of the clean-up soil standards is done by a tiered approach depending on the quality and the quantity of the ecotoxicological data. Preferable the Weight-to-evidence approach, which is based on a statistical treatment of the data, is used. If the criteria for application are not fulfilled the criteria for the next tier must applied. In total three tiers are defined. If the data do not meet the criteria for the last tier, no calculation is possible and urgent scientific research should be proposed.

Contaminated Soil '98, Thomas Telford, London, 1998, 759–760

All kind of ecotoxicological data are used together (EC_x, NOEC and LOEC). A frequency curve is made and the 25th percentiel is determined. Beneath this value, only 10 or 25 % effect data are allowed. If there is a higher percentage of effect data, and/or if other specified criteria are not met an uncertainty factor should be applied to the result. This uncertainty factor ranges between two and five.

Standards for soil invertebrates and terrestrial plants (S_{ip}) are calculated apart from standards for microorganisms (S_{mo}) . Both results are compared with each other based on following agreement :

- if $S_{ip} \leq S_{mo,}$ the clean-up soil standard equals S_{ip}
- if $S_{ip} > S_{mo}$ the clean-up soil standard is calculated as the geometric mean of S_{ip} and S_{mo} together

Results of the application of the methodology for heavy metal pollution are shown in detail on the poster.

REFERENCES

CCME (1996). A protocol for the derivation of environmental and human health soil quality guidelines. *CCME-EPC-101E, CCME, Winnipeg, Mannitoba, Canada.*

Denneman C.A.J. and van Gestel C.A.M. (1990). Bodemverontreiniging en bodemecosystemen: voorstel voor c-(toetsings)waarden op basis van ecotoxicologische risico's, *Bijlage bij rapportnr. 725201001, RIVM, Bilthoven, Nederland.*

Goyvaerts M.P. and Cornelis C. (1996). Voorstel voor normering van bodemverontreiniging bij type I-bestemming (natuur). *VITO, DIA.RB9652.*

Goyvaerts M.P. and Cornelis C. (1997). Voorstel voor normering van bodemverontreiniging bij type I-bestemming (natuur). *VITO, 1997/DIA/050 + bijlage*

ORNL (1995a). Toxicological Benchmarks for Screening Potential Contaminants of Concern for Effects on Terrestrial Plants : *1995 revision. ES/ER/TM-85/R2.*

ORNL (1995b). Toxicological Benchmarks for Potential Contaminants of Concern for Effects on Soil and Litter Invertebrates and Heterotrophic Process. *ES/ER/TM-126/R1.*

Vlaamse Gemeenschap (1995). Bodemsaneringsdecreet - Vlarebo. Decreet van de Vlaamse regering van 22 februari 1995 betreffend de bodemsanering (BS 29 april 1995, err. BS, 3 oktober 1995).

Contaminated land in Scotland: the impact and challenge of the new statutory regime

W. Sutherland

Environmental and Consumer Services Department, City of Edinburgh Council, Chesser House, 500 Gorgie Road, Edinburgh EH11 3YJ, United Kingdom

Key words: authorities' role, contaminated soil administration, environmental policy instruments, regulations, responsibility

A new statutory regime to deal with contaminated land in the United kingdom is soon due to be introduced. The new statutory regime will impose considerable technical, legal and administrative challenges to the agencies charged with its administration. The impact of the new regime is considered, within the overall context of the administration of contaminated land in Scotland, its limitations, and the problems likely to be faced in its implementation.

The existing contaminated land regime

It is probably fair to say that until now, the identification and remediation of contaminated land in Scotland has been more or less *ad hoc*. Indeed, the most effective tools to deal with contaminated land under the existing regime have tended to be reactive (development-led).

Pro-active interventions by regulatory authorities have often been circumscribed by insufficient knowledge of potentially contaminating past and present uses, poor co-ordination between agencies (and even departments of a single agency), poor knowledge of investigation techniques and remediation options, and inadequate advice from Government on the assessment and remediation of potentially contaminated sites.

Currently, pro-active action can be taken under the following:

- statutory nuisance provisions; in reality, these have never been applied in a systematic way to contaminated land
- protection of controlled waters; action to protect controlled waters (these include ground, surface, estuarine and inshore marine waters) has not generally been applied in Scotland, except where pollution becomes manifest in surface water or at a groundwater abstraction point.

The proposed contaminated land regime

The new regime, if implemented as currently proposed, will exclude the regulatory systems that are meant to protect the environment from current and future polluting activity. The new regime will only apply to sites that are already contaminated, and where alternative statutory regimes do not apply.

The primary role in the new contaminated land regime will rest with local authorities. It is intended to "reflect their existing functions under statutory nuisance procedures,

and...complement their roles as planning authorities." The new regime seeks to apply the existing statutory nuisance provisions to land in a much more systematic way, however. It will apply where there are assessed risks to health, and also where there are risks to specified ecosystems and property, and pollution of controlled waters.

A number of components are involved in the application of the new contaminated land regime:

- a requirement for inspection of its area by a local authority;
- a new definition;
- a new assessment strategy, based on the assessment of risk to specified targets (human health, specified ecosystems and property, and controlled waters);
- the allocation of responsibility for contamination (identifying the *appropriate person)*;
- the recovery of costs; and
- remediation.

Risk assessment is central to the regime. To identify a site as contaminated, there must be an identified pathway from the source of contamination, to a specific receptor or receptors.

Unusually for a statutory regime, the emphasis is on voluntary remediation of contaminated sites. Except where there is an immediate risk, there is a minimum three month time lag between the identification of a contaminated site and the appropriate person(s), and the service of a remediation notice. This is to allow negotiation between the statutory authority and the appropriate person, to encourage remediation without recourse to the statutory process.

There will be a considerable resource burden to all the regulatory agencies, in training staff and setting up administrative systems. Additionally, the costs of identifying and assessing sites will be considerable, and the identification of appropriate persons may be very difficult. The regime is designed to allow recovery by enforcement agencies of these costs in the case of contaminated sites. There is no mechanism, however, to recover the cost of assessing sites that do not fall within the limited definition of "contaminated." There will also, inevitably, be a number of contaminated sites where cost recovery is impossible or impracticable.

As yet, no additional resources have been allocated for implementation of the new regime. This is likely to create considerable difficulties for local authorities, which are already under strict financial constraints.

References

Environmental Protection Act 1990 Part IIA: Contaminated Land Draft Statutory Guidance

The Environment Committee 2nd Report (1996-97), Minutes of Evidence HC 22-II. The Stationery Office, London, 1996.

The 19th Report of the Royal Commission on Environmental Pollution, *The Sustainable Use of Soil* (Command Paper 3165). The Stationery Office, London, 1996.

QUALITY ASSURANCE FOR SITE INVESTIGATION IN THE NETHERLANDS

mr.drs. W. de Koning and drs. A.A. de Groof
VKB secretariaat, Postbus 77, 1200 AA Hilversum, The Netherlands

Key words: quality assurance, quality standards, site investigation

Summary
The results of site investigations can have a substantial impact on a wide range of activities. It is therefore very important to guarantee a high quality in this field. In The Netherlands some twenty environmental consultancies, representing around 80% of the site investigation market, have now joined the VKB, the Association of Quality assurance in Site investigation. Within this association the members are working towards a quality assurance system that will include all aspects of site investigation. These activities are conducted in cooperation with other certifying institutions.

Quality of site investigation is very important
Site investigation results can have a substantial impact on all parties concerned. Faulty interpretations can lead to substantial risks to public health. A contaminated site can also jeopardize spatial development plans when decision-makers believe that remediation cannot be carried financially by the plan. The possible magnitude of this type of impact justifies great care in securing the reproductivity and reliability of site investigation results. Both the chances of errors in site investigation and the chances of different results, given by different consultants on the same problem, have to be kept to a minimum. In The Netherlands two initiatives have been started some years ago to tackle this problem.

Two initiatives
Discussions among several governmental and industrial organizations[1] have resulted in the founding of the Association for Quality assurance in Site investigation (VKB) in June 1996. Some twenty of the larger consultancies, representing around 80% of the Dutch site investigation market, have now joined this open association.

The VKB aims to reach full quality assurance in site investigation among its members within a relatively short period. The association develops collective standards for carrying out site investigation. The members of the association oblige

---

[1] *Governmental organizations:*
VROM: Ministry of Housing, Spatial Planning, and Environment
IPO: Association of Dutch Provinces
VNG Association of Dutch Municipalities
Industrial organizations:
Stichting BSB: Foundation for Soil Remediation of Industrial Sites
ONRI: Order of Dutch Engineering Consultants.

Contaminated Soil '98, Thomas Telford, London, 1998, 763–764

themselves to apply and maintain these standards in their work, in addition to the ISO quality assurance system already used. The VKB also supervises the application of the developed protocols by its members.

Within the VKB experiences encountered by members as well as their clients are used to continuously improve the quality of site investigation. This results in the constant maintenance and optimization of the existing protocols.

The other initiative consists of the process-certification-procedure, initiated by Kiwa, a Dutch testing and research institute. This initiative was started by the publication of an assessment-guideline for the site investigation fieldwork. At present nine of the smaller consultancies comply with this guideline, winning each of them a process-certificate.

Infrastructure for quality assurance
Presently, certifying institutions are being provided with advice by several expert panels. These boards, in which all parties involved are being represented by specialists, each manage one specific certification programme. The VKB is being supported additionally in its work by a Board of Advice, in which VROM, IPO, VNG and BSB are represented. The Board of Accreditation supervises all certifying institutions.

State of affairs and future plans
Since November 1996 six VKB-protocols are available for fieldwork activities. Kiwa has produced, apart from its assessment-guideline, five product-certificates.

In the near future both organisations will develop documents for other parts of site investigation, including materials used. In 1998 the VKB and Kiwa are going to coordinate their respective activities with the following long-term goals:

- further harmonization of applied procedures and techniques
- application of improved techniques and procedures
- economical and efficient practices
- clear definition of quality.

One of the important tasks of both organizations in the near future is to further integrate their activities. As an example serves the present proposition to install a single expert panel, which will manage the various certification programmes. Organizations will find it easier to find their way through this 'one window approach'. Specialist committees will be available to the panel for the technical preparation of assessment-criteria.

With the VKB's specialists on processes in the field and Kiwa's specialists on materials used a single infrastructure can be forged with the capability to further shape quality assurance of site investigation in The Netherlands.

THE CLASSIFICATION OF CONTAMINATED MATERIAL IN HIGHWAY EARTHWORKS

P Wilson[1], J Perry[2] & J M Reid[3]

[1]Highways Agency, Geotechnics & Ground Engineering, St Christopher House, London SE1 0TE.
[2]Mott MacDonald, Foundation & Geotechnics Division, St Anne House, Croydon CR9 2UL.
[3]Transport Research Laboratory, Old Wokingham Road, Crowthorne RG45 6AU.

Key words: contaminated soil, groundwater, guidelines, human health risk, regulations, risk assessment

SUMMARY
A revision to Clause 601 of the Specification for Highway Works is proposed to improve the classification of contaminated materials in highway earthworks. The new classification is based on the concept of risk assessment and the definition of contaminated land given in Section 78 of the Environmental Protection Act.

The use of materials in highway earthworks in the UK is set out in the Specification for Highway Works (SHW) (MCHW1), seventh edition, 1991. Materials are classified as acceptable or unacceptable for a range of uses depending on their geotechnical properties. The document is written and structured to allow the maximum use of materials. At present, contaminated materials may be classified under Clause 601 as either:

Unacceptable material Class U1
ii) material, or constituents of materials, composed of the following unless otherwise described in Appendix 6/1:
f) non-hazardous materials other than those permitted in Table 6/1 and Appendix 6/1.

Unacceptable material Class U2
i) materials having hazardous chemical or physical properties requiring special measures for its excavation, handling, storing, transportation, deposition and disposal.

A classification for contaminated materials was first introduced in the sixth edition of the SHW in 1986, which included the current Class U2 definition. Class U1 (ii) (f) was introduced in the seventh edition in 1991 as a low contaminant classification. The perception of contaminated materials has changed and scientific understanding of their behaviour has increased in recent years and a revised classification is now required. This should reflect the change in emphasis from levels of contaminants in a material to assessment and management of the risks posed by the contamination on a site specific basis. Section 78 of the Environmental Protection Act, introduced by the Environment Act of 1995, includes a definition of contaminated land which reflects this approach. This definition has been incorporated into the draft revised SHW Clause 601 classification, which is given below:

Unacceptable material Class U1 shall be:
ii) material, or constituents of materials, composed of the following unless otherwise described in Appendix 6/1:
f) contaminated materials, including controlled wastes (as defined in the Environmental

Contaminated Soil '98, Thomas Telford, London, 1998, 765–766

Protection Act 1990), whose level of contamination is above that given in Appendix 6/14 [limiting values for pollution of controlled waters] or Appendix 6/15 [limiting values for harm to human health and the environment], and excluding all special wastes (as defined in the Special Waste Regulations 1996) and radioactive wastes (as defined in the Radioactive Substances Act 1993),.

Unacceptable material Class U2 shall be:

i) special waste (as defined in the Special Waste Regulations 1996) and radioactive wastes (as defined in the Radioactive Substances Act 1993).

Further information on the selection of limiting values is given in a set of Notes for Guidance (NFG). The limiting values should be derived by means of a site specific risk assessment, and details of how they were obtained should be given in Appendix 6/14 and Appendix 6/15 of the tender documents. However, there is provision for the use of generic guideline values as default values. The generic values should have themselves been produced by a risk assessment model, such as the guideline values currently under development by the Department of the Environment, Transport and the Regions (DETR). For general fills, the limiting values for harm to human health should normally be based on the commercial/industrial end use category, as there is a very low risk of exposure of the public to any contaminants in the fill. Provision for treatment of contaminated materials to render them acceptable is included, subject to a satisfactory risk assessment.

The revised classification will be issued as a draft amendment to the Specification and will be trialed in appropriate schemes. Full implementation is dependent on publication of the Statutory Guidance on contaminated land and accompanying documents on risk assessment and guideline values by DETR. The draft amendment may require revision in the light of the final, published versions of these documents. However, the basic philosophy behind the new classification is unlikely to change. It is hoped that the new SHW and NFG clauses will encourage more re-use and treatment of materials on site and less excavation and disposal.

The revised classification is currently being trialed on a major highway scheme in England. As the Statutory Guidance and guideline values have not yet been issued by DETR, default values have been taken from Table 1 of Interim guidance on the disposal of "contaminated soils" (Environment Agency, 1997). These values have not been derived by a quantitative risk analysis process and are hence somewhat conservative.

References

Environment Agency (1997). Interim guidance on the disposal of "contaminated soils". 2nd edition, 01/05/97.

House of Commons. Environmental Protection Act 1990, Section 78. Her Majesty's Stationery Office, London.

Manual of Contract Documents for Highway Works. Her Majesty's Stationery Office, London.

Volume 1: Specification for highway works (MCHW1).

SOIL REMEDIATION IN FLANDERS NEW POLICIES AND STRATEGIES

W. De Nijs [1], E. Van Dyck [1], E. Wille [1] and J. Ceenaeme [1]

[1] OVAM, Public Waste Agency of Flanders
Kan. De Deckerstraat 22-26, B-2800 Mechelen, Belgium

Key words : legislation, environmental policy instruments, land register, inventory, contaminated sites

1. Introduction

In 1995, a Decree concerning soil remediation was ratified by the Flemish government. This Decree contains some key-issues who reveal new ways to handle this issue :

- the register of polluted soils and the possibility to request a soil certificate, an extract of this register;
- the difference between historical and new soil pollution;
- the difference between obligation and liability for remediation.

2. Soil investigation

There is an obligation of investigation of soils at the moment of property transfer, on a periodical base or by closure of certain installations who can or could cause soil pollution.The authorities may also gather information as a result of its investigations into soil quality. The exploratory investigations include a limited investigation into the past history of the soil, as well as restricted sampling operations.

If these investigations indicate the presence of pollutants, the need for further soil investigation depends on comparison of the concentrations with soil cleanup values. During a descriptive soil investigation the pollution will be characterised in detail and the risk for humans and ecosystem will be defined. The aim of this examination is to give a description of the nature, quantity, concentration and origin of the contaminating substances, the possibility that these might spread, and the danger that human beings, plants and animals, as well as surface and groundwater, might be exposed to it.

3. Need for remedial operations

There is made a distinction in policy depending on the origin of the soil pollution. "Historical" soil pollution is pollution originated before the Decree came into force (29 October 1995). "New" soil pollution originates after the Decree came into force.

The clean-up of new pollution is, according to the Decree, required as soon as the soil clean-up values are exceeded. With respect to historical pollution, the decision to clean-up will depend on the actual danger to man and the environment (non quantified general criteria). So a risk-assessment aproach is followed in the descriptive soil investigation. The clean-up actions are determined in a soil remediation plan. The Public Waste Agency of Flanders (OVAM) supervises the clean-up operations.

Contaminated Soil '98, Thomas Telford, London, 1998, 767–768

4. Register of polluted soils

The information on soil pollution and soil remediation leads to the constitution of a register of polluted soils. This register serves as a data base for policy decisions and also functions as an instrument to protect and inform potential buyers of polluted soils.

The register of polluted land is open to the public. The soil certificate, an extract of the register for a specified ground, gives for the ground information concerning :

- the identity of the owner and user of the ground;
- the presence in the register;
- the existing investigations or soil remediation plans;
- the origin of the soil pollution (historical or new);
- the seriousness of the pollution;
- the presence of a clean-up obligation.

5. Obligation for remediation and liability

In the Flemish Decree a clean-up obligation rests on the operator or the owner of the land where the pollution entered the soil. This means also that the obligation does not rest on the owner of the land polluted by migration of pollutants from other property. If new pollution is concerned, the obligation exists automatically. In the case of historical pollution, the obligation only arises after the clean-up order by the government.

The Flemish Decree intoduced a non-retroactive strict liability rule and channelled the liability for the new pollution to those that caused the pollution. Recourse against other responsible parties is however possible. With respect to historical pollution, liability is determined by the rules in effect before the decree came into force.

The owner or operator of the land where the pollution entered the soil is not obliged to carry out the clean-up if he can prove that he did not cause the pollution himself (by his fault or otherwise) and that when acquiring the property, he was not and should not have been aware of the pollution. In addition is the owner for historical pollution not obliged to carry out the clean-up if he proves that the polluted land was acquired prior to 1993 and was since then exclusively used for a non-professional use although he had prior knowledge of the pollution.

6. Soil investigations and remediation plans in Flanders

The subjoined table gives a survey of the number of soil investigations and remediation plans that the Public Waste Agency of Flanders (OVAM) received in 1997. In a case where the soil contamination represents an immediate threat, the OVAM takes appropriate safety measures.

Exploratory investigations	3 400
Descriptive investigations	350
Soil remediation plans	70
Lots in the register of polluted soils	7 000

SAFETY AND HEALTH PROTECTION IN THE REMEDIATION OF CONTAMINATED SITES

Dipl.-Geol. Andreas P. Feige-Munzig,
Tiefbau-Berufsgenossenschaft, Landsbergerstraße 309, D-80687 München, Germany

Keywords: abandoned polluted areas; guidelines; health and safety; occupational safety; planning; prevention; risk assessment; .

1. GUIDELINES FOR SAFETY AND HEALTH PROTECTION

Contaminated sites, where soil, groundwater or even buildings are polluted by a wide number of hazardous substances, are being remediated to protect the environment and the human beings. Released in the remediation work, the hazardous substances constitute a serious health risk for workers.

In order to minimise this health risk, an interdisziplinary working group set up under the responsibility of the german Tiefbau-Berufsgenossenschaft as one of the statutory accident prevention and insurance institutions for the german civil engineering industry has prepared a comprehensive concept for occupational safety and health protection in the remediation of contaminated sites entitled "**Guidelines for Safety and Health Protection for Working in Contaminated Sites**". The guidelines summarise the main safety regulations and provides stipulations on the main deciding factors for preventive protection of health. One of its main ideas is the determination of responsibilities and the distribution of duties between client and contractor in planning and implementation.

2. RESPONSIBILITY OF THE CLIENT

Mainly, the client is responsable for the investigation of hazardous substances, the risk analysis and the planning of the appropriate measures for safety and health protection. The investigation of hazardous substances and risk analysis also include ascertainment of the risks emanating from biological agents, i.e. bacteria, fungi, viruses, endotoxins and parasites, in particular in the case of work on disposal sites for domestic waste or of microbiological soil remediation. The risk analysis has to consider the physical, chemical, toxic, allergenic and infectious properties of substances and biological agents, their mobility and emission behaviour. The results of the investigation and the risk analysis and, based on these, the demands on technical, organisational and personal safety measures, as well as the demands on controlling the work with measuring instruments, have to be described in a work-and-safety-plan.

3. RESPONSIBILITY OF THE CONTRACTOR

The contractor is responsible to check the work-and-safety-plan and, if appropriate, to point out inconsistencies as well as making all the necessary arrangements and taking all measures, including e.g. provision for prophylactic industrial medical check-ups and care. Based on the safety plan, the contractor must draw up operating instructions for each place of work or for each job handling hazardous substances. He has to instruct his employees in the risks typical of the project, the protective measures and rules of conduct. He has to organise fire practices and training in first-aid and to arrange for control with measuring instruments.

Contaminated Soil '98, Thomas Telford, London, 1998, 769–770

4. BASIC REQUIREMENTS OF THE PROTECTIVE MEASURES

The prime necessity in handling hazardous substances is prevention, the avoidance or minimisation of contact to the greatest possible extent, in particular in the case of cancerogenic substances. According to the ranking of protective measures, this goal should always be aimed for by means of primarily technical measures. Any residual risks should be covered by means of organisational measures and personal protective equipment. Examples of **protective technical measures** are

* sucking off the hazardous substances at the place of emission,
* continuous forced ventilation by means of fans, creating a set wind direction
* sealed drivers-cabins with air supply systems (filter- or compressed air equipment)
* use of remote-controlled appliances.

Protective organisational measures consist, for example, of dividing the remediation site into "clean and dirty areas", laying down rules of conduct under normal operating circumstances as well as in the case of "incidents" and also carrying out industrial medical check-ups. Supplying the special site installations, e.g. hygiene facilities such as "clean and dirty"-installations, decontamination facilities for vehicles and personal protective equipment, also belong to the organisational protective measures.

Related to **personal protective equipment**, the Guidelines have the following basic requirements:

* **Hand protection**: protective gloves allowing minimal permeability of the hazardous substances,
* **Foot protection**: safety gum boots,
* **Head protection**: protective helmet, with face shield as protecti on against spray
* **Disposable protective clothing** for standard use, to be selected according to its protective effect against the properties of the hazardous substances (gas-, vapor- or liquid phase, hydrous solutions, dust).

Special protective equipment such as **respiratory equipement** and in individual cases **insulating protective suits** must be readily available in accordance with the requirements of the risk analysis and used according to the specific rules for the utilisation of the different kinds of protective equipment.

5. CONTROL VIA MEASURING INSTRUMENTS

An additional item in the safety plan is the control via measuring instruments for places of work and jobs. In addition to the oxygen content of the air, places of work subject to risk of exposure to the anticipated hazardous substances, in the case of inflammable substances also with a view to the risk of explosion, must be continuously controlled with measuring instruments, either using portable monitors with direct indicators or such monitors as fixed installations at each place of work.

6. CONCLUSIONS

With regard to the aim of Safe Construction Operations the **Guidelines for Working in Contaminated Sites** offer a model for collaboration between client and contractor, which may help to provide for equal competition both within the single market and also throughout Europe. The basic idea behind the planning, preparation and implementation of measures relating to health and safety should at all times be the concept of prevention, for

Preventative Measures taken today save Medical Treatment tomorrow.

CONTAMINATED SITES FOR THE EVALUATION OF POTENTIAL TECHNOLOGIES - *CONSEPT*

R.P. Bardos[1], S. Johnson[2] and D Laidler[3]

[1]r[3] Environmental Technology Ltd, PO Box 58, Ware, SG12 9UJ, UK.
[2]Certa (UK) Limited, America House, 2 America Square, London, EC3N 2LU
[3]Parkman Environment, 307-317 Euston Road, London NW1 3AD, UK

Key words: clean-up cost, contaminated sites, data analysis, education and training, environmental technology, field test, management, programme of research, reuse (of sites), soil and groundwater contamination

SUMMARY
This brief paper outlines a Feasibility Study, which over an 8 month period in 1996/97 investigated possibilities for the development and management of a network of field scale test sites in the UK. The network would be used for research and development, and demonstration / verification of contaminated land technologies.

CONSEPT is envisaged as a network of independently owned test sites administered by a central executive. Its objective would be to facilitate the use of this network of test sites by independent projects concerned with field scale contaminated land technology R&D and the demonstration and verification of contaminated land technologies. The proposed *CONSEPT* initiative is seen as being unique in its aim to combine:

- technology demonstration and approaches to verification;
- field scale research and development;
- natural attenuation studies for contaminated sites; and
- networking and communication between the various stakeholders in contaminated land management.

To summarise *CONSEPT*'s proposed activities a draft Mission Statement was developed in the Study: *"CONSEPT [would] exist to facilitate the provision of test sites for research and development, and demonstration and verification activities financed by Public and Private Sector funders. It [would] identify and organises sites for project use. It [would] identify and present projects to site holders. It [would] collate, analyze and disseminate the information from the test sites it is responsible for".*

The contaminated land technologies of particular interest to *CONSEPT* fall into four broad categories: site assessment; risk assessment; control measures (containment and treatment); and measurement and monitoring.

The proposed objectives for *CONSEPT* were defined in the study in the context of facilitating technology use in the UK remediation market:

1. Technology research, development and demonstration at a scale in which natural heterogeneities and other processes are effective, comparing the effectiveness of

interventions as far as possible against naturally occurring processes;
2. Verification of technology performance under real conditions of field-scale heterogeneities, comparing the effectiveness of interventions as far as possible against naturally occurring processes;
3. Dissemination of information about contaminated land technology use, using *CONSEPT* to develop a community of contaminated land interests across the various stakeholders for contaminated land problems.

Three fundamental values were suggested for underpinning *CONSEPT*'s activities. *CONSEPT* should be: (1) based on sound science; (2) exploit close collaboration of all stake-holders; and (3) be consistent with national approaches and industrial interests. The Study proposed that *CONSEPT*'s R&D activities would be guided by a Research Strategy and a draft has been developed, considering three elements:

- type of site;
- type of technology (as described above); and
- research type (basic & applied)

The Study concluded that the establishment of *CONSEPT* is feasible and that the initiative is indeed needed by a number of potential stakeholders. Furthermore, *CONSEPT* could offer an opportunity for the UK to achieve both technical advantage and commercial gain from taking a co-ordinated and integrated approach to finding effective, safe and economical solutions which can be applied with confidence to the problems of contaminated land. The *CONSEPT* initiative was described as having the potential to be:

- a beacon -to inspire and draw forward suitable projects;
- a catalyst - to stimulate the development of new partnerships and new ideas for projects;
- a facilitator - to help projects find suitable sites and *vice versa*
- an advert - for UK expertise and skills and the UK approach to managing contaminated land, commanding the heights of the international debate on the sustainable development of contaminated land and being a prestigious platform for the marketing of UK expertise and technologies.

The Feasibility Study was carried out by and supported financially by A&S Associates, Parkman Environment and r^3 Environmental Technology Ltd. It was carried out with the help, guidance and financial support of the Department of the Environment, Transport and the Regions; English Partnerships; the Environment Agency, the Soil and Groundwater Technology Association and some of its individual members; and the Welsh Development Agency.

A due diligence exercise on the Feasibility Study was completed by an independent consultant early in 1998. This indicated that, whilst there is a good level of support for the objectives and benefits of CONSEPT, the network may be constrained if site and project fees are the only source of income. Other funding sources will need to be sought to develop the network. Nevertheless, implementation of 15 projects across 10 sites over 3 years was considered achievable.

SYSTEMATIC INVESTIGATION INTO 350 SITES WITH SUSPECTED WARFARE-RELATED ENVIRONMENTAL DAMAGE IN BAVARIA

Dr. B. Kaukal[1], R. Schneider[2] und Dr. J. Schäfer[3]
[1] u.[2]: Bayerisches Staatsministerium für Landesentwicklung und Umweltfragen (StMLU), Rosenkavalierplatz 2, D-81925 München, Germany
[3]: Industrieanlagen-Betriebsgesellschaft mbH, Einsteinstraße 20, D-85521 Ottobrunn, Germany

Key words: warfare-related contaminated sites, suspected areas, historical investigation, hazard ranking, risk assessment, priority lists

SUMMARY
Within the Free State of Bavaria, Federal Republic of Germany, approx. 350 sites are suspected to be warfare-related contaminated sites. Therefore a systematic procedure has been developped on the basis of historical investigation and provisional risk assessment of each site. Priorities have been set up to handle the issues. Remarks concerning organisation and financing complete the article.

KURZFASSUNG
Im Freistaat Bayern (BRD) sind rund 350 Rüstungsaltlastverdachtsstandorte bekannt. Aus diesem Grunde wurde eine systematische Vorgehensweise entwikkelt, die auf der historischen Recherche und einer vorläufigen Gefährdungsabschätzung eines jeden Standorts aufbaut. In der Folge der ersten Ergebnisse wurden Bearbeitungsprioritäten aufgestellt. Der Beitrag geht schließlich auf Fragen der Organisation und der Finanzierung ein.

RÉSUMÉ
Sur le territoire de l´État libre de la Bavière (R.F.A.), ils se trouvent environ 350 sites qui sont soupçonnés d´être pollués par des résidus d´armement. Pour répondre à ce défi, on a développé une procédure systématique sur la base des recherches historiques et d´une évaluation provisoire des risques de chaque site. Des priorités d´action ont été fixées. La contribution est complétée par des commentaires sur l´organisation et des questions de financement.

Starting point

Within the Free State of Bavaria, Federal Republic of Germany, approx. 350 sites are known for suspected warfare-related environmental damage originating from the first and second world wars. Warfare-related environmental damage must be suspected in all places used for the production, deposition or destruction of substances used for military purposes and therefore public safety and order is at risk.

Systematic procedure

Due to the large number of sites in Bavaria a systematic procedure has been set up in order to investigate suspected warfare-related environmental damage. The different sites are managed on the basis of a step by step process:

- from historical investigation to provisional hazard evaluation of each individual site (part-step 1a) and hazard evaluation of individual suspect areas within these sites (part-step 1b)
- preliminary as well as detailed investigation of suspect areas

Determination of priorities
Priorities have been set up for the order of the handling of these issues. The determination of priorities is based on a schematic hazard evaluation which is undertaken separately for the different paths "soil-(air-)human health" and "soil-water". For each of these paths assessments are carried out for emission potential (type and quantity), transmission potential (description of passability and locational factors) and immission potential (sensitivity of the protected goods and the uses). A numerical evaluation of the individual criteria shows the overall priority of the assessment. This classification does not indicate the actual existing dangers.

Results
Exactly 349 suspected sites were discovered of which 74 sites proved to be without specific warfare-related emission potential and 275 sites have to be checked more thoroughly. At present the sites with priorities 1 and 2 are being investigated more precisely by:
- accomplishing detailed inquiries in supra-regional archives
- analysing aerial photographs
- drawing maps of the local situation
- interviewing witnesses with knowledge of the period
- inquiring into local archives
- developing fundamental knowledge and instruments

Organisation
First of all the investigation of suspected warfare-related environmental damage is the task of the district administration offices (KVB) i.e. the lower administration level. They are supported by the Bavarian State Ministry for State Development and Environmental Affairs (StMLU). To operate more economically and effectively the StMLU assigned specific tasks to a private company, IABG in Ottobrunn. At mid administrative level, representatives of the 7 district governments in the state working group "warfare-related contaminated sites" are available for the KVBs to contact.

Financing
According to the Constitution of the Federal Republic of Germany the remediation of contaminated sites lies within the responsibilities of the Federal "Länder". It is, however, still disputable whether and to what extent the Federal Republic has a financial commitment regarding the necessary rehabilitation measures. Up to the present time the Federal Government has declined financial responsibility for the investigation and remediation of warfare-related contaminated sites. Until a clear legal ruling is made, only the owner of the contaminated site can be obliged to cover these expenses.

RISK COMMUNICATION FOR CONTAMINATED LAND: A FRAMEWORK FOR MANAGING PUBLIC CONCERN

R. Kemp[1], B. Valledy[1], M. Quint[1], S.J.T. Pollard[2], V. Forster[3], Y Crowther[1], R. Jeffries[1] and S. Aston[4]
[1]Dames & Moore, 26 Walker Street, Edinburgh, EH3 7HR, UK.
[2]Scottish Environment Protection Agency, Head Office, Erskine Court, Castle Business Park, Stirling, FK9 4TR, UK.
[3]Environment Agency, Steel House, 11 Tothill Street, London, SW1H 9NF, UK
[4]Environment and Heritage Service (Northern Ireland), Calvert House, 23 Castle Place, Belfast, BT1 1FY, UK

Key words: contaminated land, risk communication.

Introduction

The application of risk assessment as a framework within which to manage land contamination requires a strategy for communicating 'risk'. As other programmes have demonstrated[1-3], the key aspects are 'trust' in the management process, the communication of risk from individual sites and the extent of community involvement in the decision-making process. Clear information on risks, their nature and their determination is required. Experience has shown that when contamination and public concerns are intensified, an absence of appropriate information can lead to the breakdown of trust with those charged with managing the situation. This work, funded by the Scotland and Northern Ireland Forum for Environmental Research (SNIFFER) and the Environment Agency involved:

- a literature review with the identification of key lessons;
- the testing of public expectations of information regarding land contamination;
- the development of sample public information materials for land contamination; and
- the compilation of a draft risk communication manual to assist staff anticipate and manage risk perception issues.

Literature Review

The literature review focused on practical lessons from a wide range of research and case study material. It identified key insights and guidance of potential assistance to the future management of risk associated with land contamination in the UK. The review noted a fundamental perspective, captured by Paul Slovic in 1987: "*Lay people sometimes lack certain information about hazards. However, their basic conceptualisation of risk is much richer than that of the experts and reflects legitimate concerns that are typically omitted from expert risk assessments. As a result, risk communication and risk management efforts are destined to fail unless they are structured in a two-way process. Each side, expert and public, has something valid to contribute. Each side must respect the insights and intelligence of the other.*" Both the review and subsequent survey work endorsed the development of risk communication activities to improve awareness of the overall approach and objectives of managing land contamination. Such activities should take place at as early a stage as possible, and before specific site issues become a focus of local concern. The review identified a number of procedural and content issues important to effective risk communication.

Procedural issues:

- public involvement should follow and explain the stages of the risk assessment process so as to avoid potential suspicion that a site is being studied until the 'right' answer is found (i.e. an excuse not to remediate);

- sensitivity to the socio-economic impacts of land contamination e.g.'planning blight';
- careful explanation of why site investigations may require individuals to wear protective clothing, that could alarm the local community; and
- understanding that remediation practitioners will focus on costs and will want to ensure that sufficient resources are invested to produce a clear end result.

Content issues included several general guidelines:

- quantitative information will be expected and should be provided in a transparent manner with all assumptions and uncertainties clarified;
- explain terminology that would be unfamiliar or confusing to non-experts;
- do not trivialise land contamination risks by comparisons with other risks;
- be aware that interested parties will focus on consequences rather than probabilities of harm from land contamination;
- be aware that public perceptions of risk are contextual and will be influenced by factors, such as the perceived effectiveness of land contamination practitioners and managers, independent evidence and access to information; and
- present information clearly and using local contexts, but without distortion.

Public Information Materials

Empirical testing of risk communication leaflets, using focus groups, was undertaken. Participation was from people who had been 'exposed' to land contamination issues and those who had not. Results confirmed the reactions to risk-based information and to preferences over style and content previously recorded in the literature. The recommended contents for a generic leaflet were built on feedback from the groups, the emphasis being on clear, well presented information, emphasising the value of independent endorsement in terms of preserving and building trust and credibility. A direction was also given that the leaflet should be the minimal form of communication, and, as far as possible, should be complemented by other more direct forms of community involvement.

Risk Communication Manual

A draft risk communication manual - '*Communicating understanding of contaminated land risks*' - was developed to distil the learning from the literature review and focus groups into a user-friendly operational document of assistance to regulators and land contamination practitioners in the wider community. The draft manual provides a working guide for regulators who are not professional communicators, and can assist in the preliminary anticipation and management of land contamination issues. The manual provides:

- a simple overview of the new legislation and its requirements;
- guidance on risk perceptions and a preliminary questionnaire to assist staff in evaluating potential perceived risk amplification factors;
- guidance on how to identify interested parties in a land contamination issue;
- advice on the importance of timing of communications and the value of early dialogue and engagement and on developing key messages and other content issues;
- check-lists and tips on the variety of communication tools and community engagement options - from open meetings to facilitated dialogues; and
- case studies, management sheets and pro-formas to guide the above projects.

References

[1] Gots, R. (1994) *Environmental Risk Management Working Paper 94-5*, University of Alberta, 12pp.
[2] USEPA (1995) *Guidance for Community Action Groups at Superfund Sites*, OSWER 540-K-96-001
[3] Petts, J. (1996) *Land Contamination and Reclamation* 4(3): 171-178

ENVIRONMENTAL CRIMINALISTICS AT THE NETHERLANDS FORENSIC SCIENCE LABORATORY

E.J. Korthagen, E.J. Vermeij

Department of Environmental Criminalistics, Forensic Science Laboratory, Volmerlaan 17, 2288 GD Rijswijk, The Netherlands

Keywords: authorities' role, environmental investigations, national law, prosecution

Dutch environmental legislation

In recent years Dutch environmental law has seen a development from sectoral laws, each dealing with more or less isolated topics like soil polution, air pollution, water pollution and hazardous waste, towards a more integrated legislation. The most important environmental law nowadays is the Environmental Conservation Act. This act covers a broad range of subjects, and for instance discribes the procedures to obtain the compulsory permits for activities that are harmful to the environment. Another law is the Soil Protection Act. This, amongst others, prohibits any activities that can pollute the soil. The soil protection act also forms the basis for many regulations on the handling of manure and other organic fertilizers.

Environmental laws and regulations often contain technical criteria. Many of these are of a numerical nature. For example: a certain waste product is considered hazardous if the concentration of mercury is higher then 50 ppm. Other criteria are less concrete. Many environmental laws state general requirements of responsibility and care. The aforementioned rule about activities that can be detrimental to the soil is a good example. The penalty on emissions or discharges that pose a threat to human health is another. The law, however, does not state what exactly is a threat to human health and what is not.

Enforcement and prosecution

Enforcement of environmental law is a task for both the administrative authorities and the counsel for the public prosecution. The public prosecutor, who leads criminal investigations, is often specialised in environmental crime.

The police are involved in environmental law enforcement in two ways: the ordinary policeman is in the ideal position to notice environmental crimes of a smaller scale, mostly committed by individuals. Examples are small discharges of motor-oil into the soil and dumping of household waste. Often, but not always, cases like this can be dealth with without the assistance of the Forensic Science Laboratory.

More specialised police-officers investigate more complicated and more serious types of environmental crime, often associated with companies rather than individuals. These investigations almost always involve chemical analyses and other research by the Forensic Science Laboratory, as well as assistance from other organisations specialised in enforcing environmental law, for example the Environmental Inspectorate of the Ministry of Housing, Physical Planning and the Environment.

Contaminated Soil '98, Thomas Telford, London, 1998, 777–778

The role of the Forensic Science Laboratory

The department of Environmental Criminalistics of the Dutch Forensic Laboratory has three main tasks.

Our first main task is independant research in criminal cases in which violations of environmental law are suspected. In the larger environmental crime cases we offer advice on the possibilities and shortcomings of technical research methods, offer assistance in taking samples, perform chemical analyses and inform the investigators about certain difficulties that may arise when analytical results have to be compared to legal limits.

Probably the most important part of our casework is the interpretation of analytical and other data. If the law states numerical criteria, like concentration limits, this is mostly quite straightforward. Some difficulties may arise if samples have been taken from very heterogeneous materials, or if the law is not clear about which sampling and analytical methods should be employed. But usually these difficulties can be overcome, for instance by using the appropiate statistical methods. The situation is completely different in cases in which we are asked for an opinion on the actual damage or the hazards that an illegal activity has posed on the envirinment or human health. Such questions are asked when violations of requirements of responsible care are suspected. To answer them, expertise is required, not only on physical, chemical and biological environmental processes, but also on environmental government policy, which deal with topics like acceptable risk and general guidelines and objectives for environmental quality.

Our second task is the developpment of of reseach methods, for use in criminal investigations. Several R&D-projects have been carried out or are still in progress. One of the more important ones was the development of a sampling method for waste materials which is statistically sound, yet practicable for the police. Other projects concern chemical analysis of waste materials and methods to compare materials in order to be able to link pollution and pollutor.

Finally, our third main task is to function as a centre of expertise. Our expertise consists of scientific environmental knowledge, combined (we think rather uniquely), with criminalistic expertise. This is offered to the outside world in several ways. We participate in general environmental training at the various Dutch police training schools. We offer advice on technical investigations, either in specific individual cases or in general, in the form of guidelines published by the Forensic Science Laboratory. We also participate in committees on standardisation, for instance of analytical methods, sampling methods en terminology.

A recent example of our role as a centre of expertise is the installment of the "information desk on the Guideline for sampling and analysis in the investigation of environmental crime". In Dutch this is abbreviated to *iRMA*. The guideline on sampling and analysis offers procedures and criteria for the selection of appropate methods of sampling and analyses in criminal cases.

JAPAN'S GUIDELINES FOR SURVEYS AND MEASURES FOR SOIL AND GROUNDWATER POLLUTION, AND A NEW SYSTEM TO PROTECT GROUNDWATER FROM CONTAMINATION

T. FUKUMORITA

Water Quality Bureau, JAPAN ENVIRONMENT AGENCY, Kasumigaseki 1-2-2, Chiyoda-ku, Tokyo 100, JAPAN

Key words: groundwater clean-up, heavy metals, quality standards, soil and groundwater contamination, soil clean-up, volatile organic compounds.

Under the Basic Environment Law, in Japan, Environmental Quality Standards(EQSs) for soil pollution are set as the desirable levels of soil quality for the protection of human health and living environment. On February 21, 1994, Japan Environment Agency(JEA) added fifteen substances to the EQSs and strengthened some of the existing standard values. As a results, the EQSs are stipulated for the twenty-five substances.

Two types of soil pollution standards are set to protect two soil environmental functions:(1)purifying water and providing clean and safe water, and (2)producing healthy crops.

It is aimed that the EQSs are utilized as (1)standards to judge if the soil of a certain location is polluted , and (2)target levels for clean-up measures. However, the EQSs themselves do not have the power to enforce clean-up measures in accordance with the standard levels, and as of now there is no laws regulating the pollution of land exept that for agricultural land. For the reason, JEA and local governments are providing administrative guidance to urge polluters voluntarily take clean-up measures.

In order to facilitate the smooth execution of specific measures based on the EQSs and evaluation standards concerning soil and groundwater, in 1994, JEA enacted (1)"Guidelines for Surveys and Countermeasures for Soil Pollution Caused by Heavy Metals, etc." and (2)"Provisional Guidelines for Surveys and Countermeasures for Soil and Groundwater Pollution Caused by Organic Chlorides, etc." These guidelines includes the following contents:

(1) Heavy metals such as cadmium have specific characteristics, such as being highly absorbable into soil. For this reason, surveys should be provided by surface soil investigations and boring tests, to verify the

Contaminated Soil '98, Thomas Telford, London, 1998, 779–780

extent of soil pollution.
For countermeasures, polluted soil should be ecavated or removed according to the degree of pollution, then, isolated from the living environment by enclosed with concrete or waterproof sheeting, to prevent diffusion and influence on the groundwater, etc.

(2) Organic chlorides such as trichloroethylen often pollute the groundwater as well as the soil. These substances are volatile. For this reason, surveys should be started with investigations on the soil gas, then, soil and groundwater should be investigated by boring to verify the extent of soil pollution.
For countermeasures, where the degree of pollution is significant, pollutants should be removed by soil vapor extraction(set a well in the soil to absorb vaporized pollutants and treat the gas) or pump lifting and aeration (absorb polluted groundwater and aerate).

With respect to soil clean-up methods used in Japan, they have been largely confined to containment technologies to date. In view of those various technologies used in Europe and America, JEA is supporting development and utilization of advanced clean-up technologies that suit to Japan's conditions. Technology innovators conduct tests on contaminated sites being advised by the evaluation study committee in JEA. Results will be finally evaluated by this committee and introduced into the above guidelines.

In addition, May 1996, parts of the Water Pollution Control Law were amended and came into force on April 1, 1997, establishing a system to purify the groundwater. Local governors are empowered to issue clean-up orders to polluters who are or were proprietors of specific facilities in cases where human health is threatened by contaminated groundwater resulting from the permeation of polluted water from such facilities. The clean-up order includes not only groundwater clean-up but also contaminated soil remediation.

Further, with a view to providing comprehensive preservation measures for groundwater quality, new EQSs for groundwater came into force in March 1997. They are stipulated for 23 substances, including trichloroethylene. Given the hydrological cycle, the permissible levels of these substances are set at the same values as specified in the environmental standards for water quality control in Public Water Areas.

SITE SPECIFIC RISK ASSESSMENT FOR ECOSYSTEMS

M. Rutgers, and J. Notenboom

National Institute of Public Health and the Environment, Antonie van Leeuwenhoeklaan 9, PO Box 1, 3720 BA Bilthoven, The Netherlands

Key words: Risk assessment, risk, exposure, target value, intervention value, field experiment, contaminated soil, ecological effects, soil protection policy

SUMMARY

The need for improved risk assessment for ecosystems becomes manifest in the Netherlands, because of the small scientific basis of current procedures, the inability to remediate all contaminated sites (>60,000 'urgent' sites), and changing contaminated-soil policy. In this presentation the advantages of a TRIAD-based approach for application in site specific ecological risk assessment of contaminated soils and sediments will be discussed.

Contaminated Soil '98, Thomas Telford, London, 1998, 781–782

INTRODUCTION

According to the Dutch Soil Protection Act, soil quality is based on a two step procedure: i) comparison with generic quality standards, and ii), in the case of a serious contamination with concentrations above the 'intervention' values, determination of the priority for remediation. The latter is based on a few steps with site specific information, such as information on land usage and the surface area of contamination. Nevertheless, the site specific risk assessment procedure has a small scientific basis, because there is no account for site specific information on the exposure levels nor on the actual ecological receptors.

Recently, the Dutch government has accepted a new contaminated soil policy, which enables a landuse based approach in the case of an urgent remediation. After clean up, residual contamination should not lead to serious risks for the ecosystem and human health at that site. In this context, risk assessment is necessary to specify clean up goals. Besides these questions for improving risk assessment procedures in the context of the soil protection act, there is a growing interest in the Netherlands in methodologies for soil management (Active Soil Management), also based on site specific information.

AIM OF THE PROJECT

We have started a new project to sum up current scientific ideas on methodologies and information requirement for establishing site specific risks and development of a frame-work for risk assessment. Besides the use of site specific criteria with respect to the presence of contaminants (exposure assessment) lines of research focus on whether it is possible to include an effect (hazard) assessment in the site specific risk assessment procedure. In addition to site specific information on soil characteristics and chemical appearance of contaminants, public awareness and scientific arguments have forced the inclusion of other information sources such as toxicological (bioassays) and ecological (field ecological observations) information to be used into the risk assessment procedure. A TRIAD-based approach, which has been successful for risk assessment of surface waters and sediments (Chapman, 1986), would suit the inclusion of three sources of information:

1. chemical appearance including exposure assessment (bioavailability considerations taken into account),
2. ecotoxicity measurements via bioassays to cover unknown contaminants or mixture effects, and
3. field observations on relevant ecological receptors for effect assessment.

It is the combination of different fluxes of information which is considered to be especially valuable for site specific risk assessment, compared to focusing on e.g. site specific chemistry and general laboratory toxicity data alone. We are currently in-vestigating the possibilities for introducing a quantitative TRIAD-based approach for soil and sediment systems.

Chapman PM. 1986. Sediment quality criteria from the sediment quality TRIAD: an example. *Environ. Toxicol. Chem.* 5:957-964.

TARGET VALUES AND BACKGROUND LEVELS IN THE NETHERLANDS: HOW TO DEFINE GOOD SOIL QUALITY

Frank P.J. Lamé, Henk Leenaers

TNO-MEP, Department of Environmental Quality, P.O. Box 342, 7300 AH Apeldoorn, The Netherlands

Key words: background levels, quality of the soil, target values

FORMULATION OF THE PROBLEM

The target values in the Netherlands are based on (natural) background levels and on negligible risk concentrations [1]. The relation with the background levels is variable for the individual compounds. For the heavy metals the relation is relatively well known, while only little information is available on background levels for organic compounds. The target levels for the heavy metals are high percentiles of natural occurring concentrations, varying between 83 and 94% [2, 3]. Thus there is a 6 to 17% probability that the target level for a heavy metal is exceeded in a natural soil. As the evaluation of "good" soil quality is based on each individual compound analysed, the probability of exceeding a target value, and therefore exceeding "good" soil quality, will rise significantly when analysing for instance 8 heavy metals. This could be solved by simply raising the target values. However, due to the relation with negligible risk, for most compounds this is not acceptable. Furthermore, the original data were measured 15 years ago and should preferably be updated.

INVESTIGATION OF THE BACKGROUND LEVELS

More recently, several of the Dutch provinces installed a soil quality monitoring network. The data from these networks were studied in order to define the background levels for both organic and inorganic compounds [4].

Obtaining a correct data set from these networks was a problem because the monitoring networks are partly based on different principles. As a result, part of the information was incomparable. A selection of the data had to be made, rejecting data that appeared to deviate significantly due to its origin (scale, soil use, depth, etc.). The resulting set of data was used to study the background concentrations.

For the heavy metals, the results are approximately comparable to the results of the study in 1983 [2]. For the organic compounds, including PAH, PCB's and several specific pesticides, a large part of the measurements appeared to be below the detection limits. This interfered the statistical analysis of the data, specially in those cases where the target values are close to, or even below, the detection limits. Additionally only a limited number of results was available for the organic compounds. Table 1 provides statistical characteristics for some of the compounds.

It was concluded that, when comparing analytical results with target values, the relation of these target values with the background levels should be taken into account. As the quantification of the background levels depends on a large number of factors (scale, soil use, depth, etc.), these same factors should apply to the analytical results that are evaluated. In relation to the now available information on background levels, soil quality must be evaluated using mixed samples from a soil volume of approximately 1250 m^3.

Table 1: Background levels for a limited number of compounds in mg/kg on the scale of the whole Netherlands (TV = target value)

compound	mean	standard deviation	median	90-percentile	% > TV	target value[2)]
PAH	0,57	1,13	0,27	1,06	15	1
As	n.v.t.[1)]	n.v.t.[1)]	<	14,0	<1	29
Hg	n.v.t.[1)]	n.v.t.[1)]	<	0,20	5	0,3
Cd	0,44	5,0	0,20	0,50	5	0,8
Cr	13,6	11,2	9,0	29,3	<1	100
Cu	13,2	13,1	11,0	22,0	6	36
Ni	n.v.t.[1)]	n.v.t.[1)]	2,0	18,0	<1	35
Pb	27,2	38,4	20,0	46,0	2	85
Zn	46,5	108	32,9	81,8	5	140

< below or equal to detection limit

1) More than 30% of analytical results below detection limit

2) Target values for a soil with 25% clay and 10% organic matter

ALTERNATIVE EVALUATION OF GOOD SOIL QUALITY

The mentioned soil volume that should be tested based on a mixed sample does already implicate that, due to the mixing of samples, fewer samples will exceed the target values. Nevertheless, the testing of more than one compound would still result in a larger probability of exceeding a target value. Therefore, different methods for evaluating soil quality were investigated, using the data from the provincial networks [5].

It was assumed that the percentage of soils exceeding the reference values should be constant, no matter how much compounds would be involved in the evaluation. To fulfil this condition, for each compound a correction factor was introduced, defined as the quotient of the 90 percentile of the of background concentrations and the target value. When the 90 percentile is larger than the target value, the correction factor is used in the evaluation. For those compounds at least 90 percent of the evaluated background soils would satisfy when evaluating the soil on one compound.

To keep a constant percentage of "good" soil when the evaluation is based on more than one compound, it was proposed to evaluate groups of compounds, for instance the evaluation of all of the heavy metals. In this method, a small exceeding for one compound can be compensated with the low concentration of another compound.

REFERENCES

[1] J.G. Robberse, C.A.J. Denneman (1993) Do target values help to protect the soil?, F. Arends *et al.* (eds.) Contaminated Soil '93, Kluwer Academic Publishers, pp 373-382

[2] Th. Edelman (1984) Achtergrondgehalten van stoffen in de bodem, Reeks Bodembescherming 34, Sdu (in Dutch)

[3] F.P.J. Lamé (1994) Een interim protocol voor de toetsing van partijen grond, TNO report R 94/207 (in Dutch)

[4] F.P.J. Lamé, G. Frapporti, H. Leenaers, H.M.C. Satijn (1996) De kwaliteit van de vaste bodem in Nederland, TNO report MEP-R 96/424 (in Dutch)

[5] F.P.J. Lamé, H. Leenaers, H.M.C. Satijn, G. Frapporti (1997) Toetsen aan de streefwaarde, TNO report MEP-R 97/474 (in Dutch)

THE IMPACT OF MICROPOLLUTANTS FROM NON-POINT SOURCES ON SOIL QUALITY IN THE NETHERLANDS

R.O.G. Franken

National Institute of Public Health and the Environment, P.O. Box 1, NL-3720 BA Bilthoven, The Netherlands.

Key words: quality of soil, governmental directives, target value, heavy metals, organic contaminants, monitoring

Introduction

In a literature survey to assess the accumulation of micropollutants in activities regulated by the General Administrative Order (GAO) of the Dutch Soil Protection Act, seven GAOs were considered: use of manure, use of other organic fertilisers, building and construction materials, storage of waste, dredging sludge, infiltration of fresh water and disposal of waste water. The inorganic micropollutants considered for the survey were Cd, Cr, Cu, Hg, Ni, Pb, Zn, and As; the organic micropollutants included PAHs, PCBs and chlorophenols (Franken et al., 1998). The main aim was to determine by means of a critical load approach, if the annual accumulation of micropollutants from activities regulated by the GAOs would cause exceedance of the Dutch target values within a period of 100 years. A secondary aim was to evaluate this critical load approach as described and used in earlier RIVM studies (Lijzen and Franken, 1996a and b).

Critical loads

In this approach the actual annual loads to soil ($kg.ha^{-1}.yr^{-1}$) from the activities mentioned above are compared with critical loads for micropollutants. Critical loads are calculated with a model called SOACAS and represent the annual loads which will prevent the target value for soil being exceeded for a defined time period. The SOACAS model is based on a simple analytical solution for the accumulation of micropollutants in one completely mixed soil compartment as a function of the soil input. The model accounts for the distribution of micropollutants between liquid and soil phases of the soil, and employs linear approximations for plant uptake and leaching. Critical loads have been calculated for both a period of 100 years and for an infinite time frame for several combinations of soil type and land use. A similar approach is described by TNO and SC-DLO (De Vries and Bakker, 1996; Bakker and De Vries, 1996) and discussed in an international setting (UN ECE, 1997).

Accumulation of micropollutants

In general, it was found that often combinations of sources had to be considered. On arable land, for example, the main contribution of zinc is from fertilisers. However, besides this source, atmospheric deposition and additives used in pesticides make a relevant contribution. The conclusion is that additional policy measures will have to be generated to avoid accumulation of micropollutants exceeding the Dutch target levels for soil and groundwater.

Especially with respect to the copper and zinc content of manure from pigs, and zinc in compost, sharp emission reduction is necessary. For each of the GAOs recommendations considered for advanced research, monitoring and policy have been proposed. For example, it is recommended to monitor micropollutants in manure annually and to do more research on the natural attenuation of PAH in dredged sludge applied to agricultural land. In the international context, agreement on emission reduction of atmospheric deposition (heavy metals and persistent organic pollutants), and on monitoring its progress, is of importance. This is vital, as atmospheric deposition is a main source of pollution in nature conservation areas and a relevant additional source of several micropollutants on agricultural land.

Reconsidering the critical load approach

The annual input of micropollutants is compared with critical loads. However, these critical loads do not safeguard protection of groundwater. Field studies in the Netherlands indicate that relatively mobile metals like cadmium and zinc often cause the Dutch target values for groundwater in the shallow groundwater to be exceeded. To avoid accumulation of micropollutants in groundwater where target values are exceeded, the critical pore-water level is introduced. This critical pore-water level is a measure of the potential groundwater load, which, for relatively mobile metals like cadmium and zinc, should be used to avoid groundwater contamination above target levels.

For evaluating the potential contamination of and damage to growth of plants and livestock (to prevent problems with the quality of meat and milk), agricultural signal values have been used. For all micropollutants considered, the Dutch target values were, in general, found to be lower than the agricultural signal values. For the micropollutants considered, the Dutch target values can be concluded to prevent adverse effects to growth of plants and livestock.

References

Bakker, D.J. and W. de Vries (1996)
Manual for calculating critical loads of persistent organic pollutants for soils and surface waters. TNO-MEP, Apeldoorn, The Netherlands. Report R 96/509.

Franken, R.O.G., H.A. Vissenberg and W.J. Willems (1998)
Emissions of micropollutants to soil from sources restricted by GAOs.
RIVM report no. 716601003, (in Dutch) Bilthoven, the Netherlands.

Lijzen, J.P.A. and R.O.G. Franken (1996a and b)
Critical loads for priority pollutants. Part 1 and 2. RIVM report no.75810015 and 715810017 (in Dutch), Bilthoven, the Netherlands.

Vries W. de and D.J. Bakker (1996)
Manual for calculating critical loads for heavy metals for soils and surface water.
DLO Winand Staring Centre, SC report 114. Wageningen, the Netherlands.

UN ECE (1997)
Workshop on critical limits and effect-based approaches for heavy metals and persistent organic pollutants. Workshop report. UN ECE convention on long-range transboundary air pollution. Bad Harzburg, 3-7 November 1997.

Theme C: Investigation and characterization, behaviour and fate of contaminants and analyses

Physical/Chemical Treatment of Contaminated Soil to Enhance the Biological Availability of Hydrophobic Compounds

L.T.C. Bonten, J.T.C. Grotenhuis and W.H. Rulkens

Subdept. Environmental Technology, Dept. AEST, Wageningen Agricultural Univ., Bomenweg 2, 6703 HD Wageningen, Netherlands
tel. +31-317-483344, fax. +31-317-482108, e-mail luc.bonten@algemeen.mt.wau.nl

Key words: PAH, bioavailability, sorption, solvents, thermal treatment

Introduction

Biological decontamination of soil, contaminated with aged hydrophobic organic contaminants (PAHs, oil, etc.) has not always been successful due to low degradation rates and high residual concentrations that do not meet the legal guidelines. This problem, indicated as a limited bioavailability, is mainly caused by a slow desorption of the contaminants out of the soil particles and not by a low microbial degradation rate. The aim of this study is to try to increase the desorption rate of hydrophobic contaminants in the soil by the use of two different short pre-treatments of the soil: heating of the soil and soaking with an organic solvent. Both an increase in temperature and the addition of an organic solvent lead to an increase of the solubility, a decrease of the partitioning coefficient and an increase of the effective diffusion coefficient. Therefor these pre-treatments may lead to a fast dissolution of the contaminants in the bulk liquid phase. After a rapid cooling down of the soil or a fast removal of the organic solvent, sorption of the contaminants at probably better biological available sites occurs, which may lead to a situation which is comparable with a fresh contamination.

Experimental

The effects of heating and soaking on the biological availability have been determined on both laboratory and industrial PAH contaminated soils. The laboratory contaminated soils was a clayey contaminated with phenanthrene and pyrene. The industrial contaminated soils was a classification sludge from a former gas plant site contaminated with coal tar.
With thermal pre-treatment, different temperatures, timespans and moisture contents were tested. Different solvent-soil ratios were tested with soaking as a pre-treatment.
After heating or soaking of the soils the biological degradation rates of the contaminants were determined in soil slurries at 30 °C. Because a pre-treatment can lead to inhibition of the microbial population in the soil, inoculum was added before degradation. At determined moments, the concentration of PAH compounds in the soil slurries was determined by extraction with acetone and analysis with HPLC. Further the oxygen concentration in the headspace was monitored to ensure that biodegradation was not oxygen limited.

Contaminated Soil '98, Thomas Telford, London, 1998, 789–790

Results and discussion

In figure 1 the degradation of pyrene in industrial contaminated classification sludge after thermal treatment and soaking and in laboratory contaminated clay after thermal pre-treatment are shown.

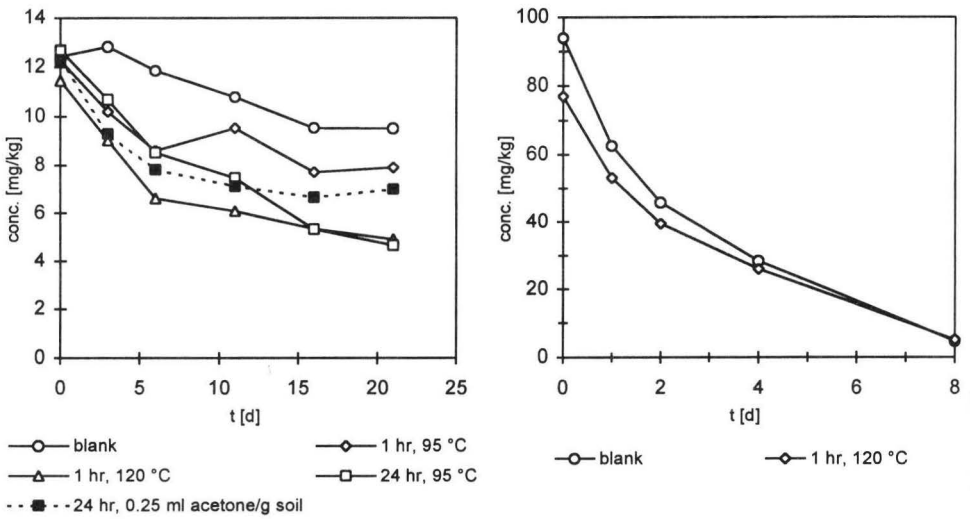


Figure 1. Degradation of pyrene in industrial contaminated soils (left) and laboratory contaminated soils (right) after thermal pre-treatment and soaking

From figure 1 it can be seen that both heating and soaking as a pre-treatment can enhance the biological degradation of pyrene in industrial contaminated soil. Similar results were found for other PAH compounds. Further can be seen that an increased temperature or an increased timespan of the thermal pre-treatment even more enhanced the degradation.
In the laboratory contaminated soil no decrease of the residual concentration was observed after a thermal pre-treatment. Probably, due to a fast and nearly complete degradation of the PAHs in the laboratory contaminated soil without a pre-treatment, heating could not further enhance the biological degradation in these soils.

Calculations have shown that the increase of the biological degradation after a pre-treatment can not be attributed to an increase of the solubility of the PAHs during heating or soaking, as this increase was calculated to be too small. The most probable cause of the increased bioavailability is a continuous redistribution of sorbed PAHs during the pre-treatment, due to increase in the effective diffusion coefficient.

Conclusion

A thermal pre-treatment and soaking with an organic solvent lead to a redistribution of sorbed contaminants, in such a way that initially non-available contaminants sorb a better available sites after the pre-treatment. These results offer a good perspective for the bioremediation of soils which can hardly be treated biologically yet, due to high residual concentrations or low degradation rates.

Degradation of polycyclic aromatic hydrocarbons (PAH): pollutant accessibility and efficiency of soil microflorae.

F. Haeseler [1,2], D. Blanchet [1], V. Druelle [3], P. Werner [4], J.P. Vandecasteele [1]

1, Institut Français du Pétrole, Rueil Malmaison, France
2, Technologiezentrum Wasser, Karlsruhe, Germany
3, Gaz de France, La Plaine Saint Denis, France
4, Technische Universität Dresden, Dresden, Germany

Key words: PAH (polycyclic aromatic hydrocarbon), gasworks, analytical methods, biodegradability, bioavailability, leaching behavior, environmental risks.

Overall characterization of total organic pollution of former manufactured gas plant soils was performed using a pyrolysis/oxidation technique (Rock-Eval) directly on soil samples and GPC/FID on solvent soil extracts. The results showed for different soils that the PAH are associated to a heavy non extractable fraction, typical of coal tar (Figure 1).

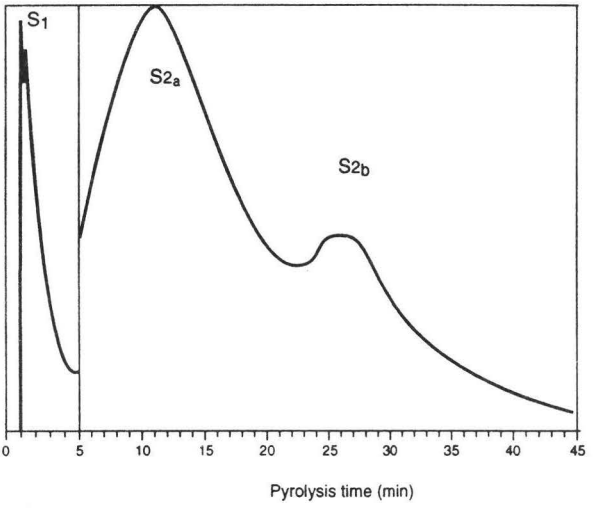


Figure 1: Rock Eval pyrogramme from a former MGP soil.
S1: volatile hydrocarbons (T≤200°C); S2a: distillable hydrocarbons (200°C≤T≤350°C); S2b: hydrocarbons susceptible to thermal cracking (350°C≤T≤600°C); S4: residual organic carbon (not presented).

A laboratory-scale methodology for the determination of PAH degradation in soils of former manufactured gas plants was also developed. Experiments were carried out in stirred reactors containing 1L soil suspension. The contaminated soil samples were carefully homogenized and detailed characterization of pollutant content was performed. Degradation progress was monitored by O_2 consumption using electrolytic respirometry equipment (Sapromat®, Voith, Germany). After 3 months of biological treatment, the residual PAH content was determined by gas chromatographic analysis of solvent extracts of soil slurries. The results, which were quite reproducible, are summarized in Table 1, and led to the following conclusions:

- only 40-45 % of PAH were degraded, higher PAH being the least susceptible to degradation,

- similar degradation percentages were observed in soils of various manufactured gas plants exhibiting widely different PAH contents,
- the contaminated soils usually contained microflorae that were active for PAH degradation,
- the degradative capacity of the indigenous microflorae was not the cause of the limited degradation observed in soil slurries. In similar conditions, these microflorae were found able of extensive degradation of PAH including 5 and 6 cycles compounds provided that PAH were made available to the bacterial microflorae either as mixtures of pure crystalline PAH or as coal tar films on glass beads.

	degradation [%]							
	Manufactured gas plant soils						Coal tar	Mixture of pure compounds
PAH	Soil 1	S.D. [1]	Soil 2	S.D. [1]	Soil 3	S.D. [1]		
2 cycles	nd [2]	-	nd [2]	-	nd [2]	-	100.0	100.0
3 cycles	81.4	*4.1*	79.9	*4.9*	88.9	*5.5*	96.0	99.0
4 cycles	56.6	*9.6*	57.1	*4.8*	67.1	*6.4*	67.0	91.0
5and 6 cycles	8.1	*3.9*	16.0	*3.3*	23.1	*5.5*	52.0	55.0 [3]
Sum of the 16 PAH [4]	41.9	*6.8*	39.7	*3.9*	52.9	*5.0*	84.0	-

Soil 1: [7,0 g PAH/kg soil]; Soil 2: [1,0 g PAH/kg soil]; Soil 3: [0,5 g PAH/kg soil]
Coal tar: 650 mg in reactor, with 13% PAH (w/w)
Mixture of pure compounds (11 PAH): 116 mg in reactor

[1]: Standard deviation calculated on series of at least 5 experiments

[2]: not determined (very low concentration of naphthalene)

[3]: Benzo(*e*)Pyrene

[4]: 16 unsubstituted PAH identified as priority pollutants by U.S. EPA

Table 1: PAH degradation in stirred reactors.

These results demonstrate that the transfer of PAH from the heavy organic matrix of coal tar particles to the aqueous phase is limited, even in efficiently stirred soil suspensions. In these conditions, the limited accessibility of PAH to bacteria clearly was the major cause of their incomplete biodegradation.

Furthermore, contaminated soils were found to display different capacities to transfer PAH to water by lixiviation. However in all cases, these transfer capacities became extremely low after biological treatment.

References:

M. Bouchez, D. Blanchet, B. Besnainou, J.-Y Leveau and J.-P Vandecasteele (1997) Kinetic studies of biodegradation of insoluble compounds by continous determination of oxygen consumption, *Journal of Applied Microbiology, 82, 310-316.*

M. Bouchez, F. Haeseler, D. Blanchet and J.-P Vandecasteele (1998) Efficiency of defined strains and soil consortia in biodegradation of polycyclic aromatic hydrocarbons (PAH): cometabolism and metabolite accumulation, *submitted*

Ramaswami, A. and R.G. Luthy, (1997) Mass transfer and bioavailability of PAH compounds in coal tar NAPL-slurry systems. 1. Model development, *Environmental Science & Technology, 31, 2260-2267*

CONTAMINATION OF AQUIFER A COUSED BY LAGOONS WITH LIQUID WASTE

A. Belic[1], B. Dalmacija[2] and S. Belic[1]

[1] Fac.of Agriculture, Inst.for Water Management, Novi Sad,Trg D.Obradovica 8,YU
[2] Fac.of Science, Inst.for Chemistry, Novi Sad, Trg D.Obradovica 3, YU

Key words: Agriculture, aquifer A, contaminated sites, wastewaters, computer model

SUMMARY

The paper deals with quality changes of aquifer A influenced by wastewater from pig breeding farms discharged in lagoons. Three experimental fields (A, B and C) have been established to obtained a complete insight into the changes of aquifer A quality in the vicinity of lagoons. Investigation results are pointed out changes of aquifer A quality in the vicinity of lagoons comparing with natural aquifer A. With regard to aquifer A quality, progress of pollution originated from lagoons are perceived. The faster migration of conservative pollutants than nonconservative are recorded. Those results are confirmed by applied mathematical model.

INTRODUCTION

The development of Vojvodina Province is most directly related to the intensive works in agriculture. This is distinguished specially in field of pig breeding which has been characterized by construction of large-capacity farms involving wet discharge technologies. Inappropriate solutions to the treatment and disposal of the generated wastewaters are present. In the majority of cases such wastewaters are temporarily stored in the special lagoons, which are not adequately designed. The lagoons represent the simple basins dug in the ground, with no appropriate isolation. In that way the lagoons have become sources of environmental pollution.

The aim of these investigation is to define aquifer A quality change influenced by wastewater from pig breeding farms discharged in lagoons. Seasonal observation of characteristic wastewaters quality parameters into lagoons (waste disposal sites) and aquifer A quality change around, during three years, are the base for dependence identification between them, within existing natural and antropogenic factors.

MATERIAL AND METHODS

To determine the characteristics of the wastewaters in the lagoons, water samples have been taken four times a year during a three-year period. In these samples were analyzed twenty parameters. To monitor the changes in composition of aquifer A, ten wells on experimental fields were drilled (three on fields A and B, four on field C). Physical and chemical characteristic of aquifer A samples were carried out analyzing the same parameters as in wastevaters. Natural aquifer A have been determined analyzing quality changes on chosen reference wells (B-360, B-385), in order to make comparations with regime around lagoons. The model for simulation spatial and time changes in the concentration of conservative and nonconservative pollutants in aquifer A have been developed.

Contaminated Soil '98, Thomas Telford, London, 1998, 793–794

RESULTS AND DISCUSIONS

On the basis of the obtained results it can be concluded that the wastewaters from the pig breeding farms are weakly alkaline, highly mineralized, and with substantial organic load. Of inorganic substances are especially characteristic the contents of chloride and sodium, though significant contents of sulfate have also been found. High content of nitrogen, of which the highest concentrations are present in the form of ammonium ion, formed as a result of decomposition of organic matter in the presence of bacteria. Naturally, the conditions and duration of wastewater storing in the lagoons influence the value of this parameter (Muck & Steeenhuis 1981).

The effect of the lagoons on the quality of aquifer A was monitored by measuring the corresponding parameters, viz. TDS, COD, and contents of Na, K, Cl, and NH_4, characterizing the influent on the one hand, and that are being important from the aspect of agricultural production and water supply on the other. The changes in Cl content and COD value are considered as being representative for the conservative and non-conservative pollutants.

Chlorides concentrations were mostly higher on experimental fields, compared to those measured for the reference wells, except for the most distant wells, such as BT-3 on the location B and BM-3 and BM-4 on the location C. The mean level in the aquifer A can be correlated with the chloride concentration (the lower the water table, the smaller the concentration) on the location B, and partly on the location A (wells BI-1 and BI-2), whereas on the location C this was not pronounced, most probably because of bigger depths and insignificant variations of the aquifer A level.

The *COD* values were mainly low, indicating that organic pollutants from the lagoons did not reach the aquifer A. Such a state was probably a consequence of a relatively short period of the potential influence (the time of lagoons operation), as well as of a high degree of degradation of organic matter in the upper soil layers. In the case of the narrow belt around the lagoons on the location C, the registered high values of COD suggest that organic pollutants, whose level in the lagoons is very high, have penetrated to the aquifer A. Most probably, such a situation has been partly due to a relatively high filtration coefficient of the meadow soil on the location C ($1x10^{-4}$-$1x10^{-6}$ cm/s).

The basis of the model form the equations concerning the elements of transport processes described by Hoeks (1981) and Rijtema (1987). The model was applied to simulate the spatial and time variation of chloride (Cl), and chemical oxygen demand (COD). A comparison of the results obtained by applying the model for all investigated locations with the results of field measurements show that this model may be used to obtain a satisfactory indication of the transport of conservative and nonconservative pollutants originated from a pollution source (lagoon) into the aquifer A.

REFERENCES

Hoeks J. (1981) Analitical solutions for transport of conservative and nonconservative contaminants in groundwater systems. *Technical bulletins, new series 2: 12, ICW.* Wageningen.

Muck R.E. & Steenhuis T.S. (1981) Nitrogen losses in free - stall dairy barns, *4th International Symposium on Livestock Wastes ASAE*, St Joseph, MI, pp.406-412.

Rijtema P.E. (1987) *Groundwater quality modeling.* I.H.E., Delft.

THE PERFORMANCE OF DIAGNOSTIC CHEMICAL INDICES FOR OIL-CONTAMINATED SITES

Martin Whittaker[1] and Simon J. T. Pollard[2*]

[1]Golder and Associates Limited, 2180 Meadowvale Boulevard, Mississauga, Ontario, Canada, L5N 5S3
[2]Scottish Environment Protection Agency, Head Office, Erskine Court, The Castle Business Park, Stirling, Scotland, FK9 4TR

Key Words: Biodegradation, oil products, microcosms, monitoring, natural attenuation

Introduction

A detailed analysis of heavy oils at contaminated sites is often required for hazard identification, risk assessment, remedial option analysis and liability apportionment reasons. Monitoring oil biotransformation involves quantifying the loss of facile components relative to 'conserved' compounds resistant to microbial attack; often expressed in the form of a weathering (or biotransformation) index. Ratios of certain biomarkers, sometimes referred to as oil (or source) correlation indices, are also used in a diagnostic mode to associate contamination events with specific sources. Here, the performance of selected oil biotransformation and diagnostic source indices for three well-characterised oils is evaluated in a soil microcosm study. Ballast oil, a North Sea Crude oil and a No.6 Fuel Oil were separately mixed with a sandy-loam and monitored for a period of 9 months under optimal biotransformation conditions. Each oil was sampled in triplicate at 0-, 2-, 4-, 8-, 16-, 32-, 64-, 128- and 256-days after initial application of the oil. Environmental analysis comprised: (i) quantitation of solvent extractable material (SEM), to allow the reduction in contaminant loads to be monitored; (ii) column chromatographic fractionation, to allow variations in class fractions to be determined; and (iii) detailed component analysis of saturate fractions by GC/MS, to allow the performance of weathering and source indices to be evaluated in full.

Results

Oil Compositional Changes. For the Ballast oil (Figure 1), SEM decreased steadily over the first 8 to 16 days of the study by approximately 30 $\%^{w}/_{w}$. A similar pattern is seen in the Crude oil microcosms. From an initial soil loading of 20 g of oil / kg dry soil, this represents a typical microbial degradation rate of 0.05 g oil / kg soil / day. No significant reductions in SEM were observed for No.6 Fuel Oil in this study. Column fractionation results showed that the average $\%^{w}/_{w}$ of saturates decreased for each of the extracts (from 74.6 ± 0.9 $\%^{w}/_{w}$ to 23.2 ± 3.4 $\%^{w}/_{w}$ for the Ballast oil (Figure 1), from 91.7 ± 0.8 $\%^{w}/_{w}$ to 70.1 ± 2.9 $\%^{w}/_{w}$ for the Crude oil and from 36.9 ± 1.2 $\%^{w}/_{w}$ to 22.0 ± 2.3 $\%^{w}/_{w}$ for the No.6 Fuel Oil), whilst the average proportions of polars and asphaltenes concomitantly increased. With the exception of the Ballast oil-treated soils, aromatic contents of extracts did not vary substantially. For this oil, the $\%^{w}/_{w}$ of aromatics, polars and asphaltenes in treated soil extracts increased from 12.5 ± 0.9, 8.6 ± 0.4 and 4.3 ± 0.3 at 0 days to 23.0 ± 2.2, 31.3 ± 5.0 and 22.5 ± 4.3 after 256 days, respectively. For the Crude oil-treated soils, polar and asphaltene class fractions increased from an initial content of 3.5 ± 0.4 $\%^{w}/_{w}$ and 2.9 ± 0.6

* current address: Risk Analysis Manager, National Centre for Risk Analysis and Options Appraisal, Environment Agency, Steel House, 11 Tothill Street, London, SW1H 9NF

Contaminated Soil '98, Thomas Telford, London, 1998, 795–796

$\%^{w}/_{w}$, to 9.0 ± 2.4 $\%^{w}/_{w}$ and 18.2 ± 3.8 $\%^{w}/_{w}$, respectively. Similarly, for the No.6 Fuel Oil-treated soils, the $\%^{w}/_{w}$ of polar and asphaltene class fractions increased from 12.7 ± 0.9 and 14.6 ± 1.4 to 21.6 ± 3.1 and 26.1 ± 2.9, respectively.

Index Performance. A performance assessment of selected candidates for diagnostic indices indicated that for the Ballast oil and Crude oil, results the most sensitive weathering index was [*n*-alkanes:17α(H)21β(H)-hopane], which after 256 days decreased from an initial mean value of 748.9 ± 37.7 to 8.5 ± 1.0 for the Ballast oil and from 81.9 ± n/d to 18.1 ± 14.2 for the Crude oil. ANOVA of the values of [*n*-alkanes: 17α(H)21β(H)-hopane] over the 256 days showed that the variation was statistically significant. Both of these results provide evidence that phytane becomes depleted in heavily biotransformed oils, and indicates that the weathering index [C_{18}:phytane] may be used to monitor oil biotransformation reliably only in light-to-moderately weathered samples. The relationship between the measured decrease in saturates abundance (mg/g soil) and the predicted decrease in saturate class abundance using each index was examined. For the Ballast oil [$\Sigma C_{14\text{-}28}$:C_{24}tetracyclic terpane] index, the calculated and actual abundancies were generally within 0.5 mg/g, whereas for [*n*-alkanes: 17α(H)21β(H)-hopane index, the difference between the two values was found to be up to *ca.* 3 mg/g. For the Crude oil, the index that most closely matched the actual loss in saturates was the [*n*-alkanes: 17α(H)21β(H)-hopane] index.

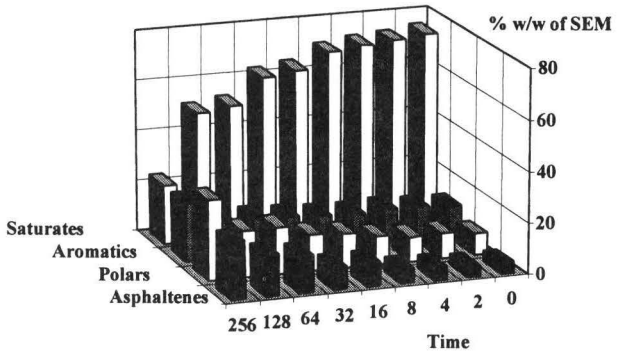


Figure 1:

Class Fraction Variations in Ballast-Oil Amended Soils

The most reliable source indices were found to be those comprising of ratios of hopane isomers, specifically: (i) the [17α(H)21β(H)-norhopane:17α(H)21β(H)-hopane] for the Ballast oil and Crude oil, which exhibited mean values of 0.7 ± 0.1 for the Ballast oil, and mean values that varied between 0.6 and 0.7 (precisions less than 0.05) for the Crude oil; (ii) the ratio of 17α(H)21β(H)-homohopane (22S) and 17α(H)21β(H)-homohopane (22R) isomers, [22S:22R], which gave a mean value of 1.3 (precisions less than 0.05) at every sampling point for the Crude oil microcosms, and; (iii) [17α(H)21β(H)-bishomohopane:17α(H)21β(H)-methylhopane], which varied between 1.3 and 1.6 (precision up to 0.1) for the Crude oil microcosms. The results also show that the [pristane:phytane], [phytane:17α(H)21β(H)-hopane] and [C_{23}tricyclic terpanes:C_{24}tricyclic terpane] indices remained fairly constant over the initial stages of oil biotransformation but then decreased significantly in value. These results are of potential values in resolving liability disputes as well as assisting in a more general sense with site investigation, risk assessment and remedial options analysis.

Bioavailability of PAHs in Soil and Ecotoxicological Considerations

A.P. Loibner, O. Szolar, M. Schlegl, M. Gartner and R. Braun
IFA-Tulln, Universität für Bodenkultur
Konrad Lorenz Str. 20, A-3430 Tulln, AUSTRIA

Keywords: bioavailability, ecotoxicological, PAH, biodegradation, extractability

SUMMARY
The influence of organic matter content and age of PAH-spiked soil on biodegradability, toxicity, and supercritical fluid extractability was investigated and discussed. Results indicate significant correlation of these bioavailability related measures.

INTRODUCTION
As numerously described in literature the biodegradation of PAHs in soil is influenced by their bioavailability. The phenomenon of bioavailability is determined by the concentration and the chemical nature of the respective PAH, the composition of the soil (in particular soil texture and organic matter content), the age of the contamination (in general considered to be a few decades) and the presence of additional pollutants like e.g. the tar oil matrix at manufactured gas plant sites.
Furthermore bioavailability will influence ecotoxicological effects exhibited by PAH-contaminated soil. However, microbial accessibility to PAHs in soil may differ from pollutant accessibility of ecotoxicological testorganisms. Thus the following work compares bioavailability, toxicity, microbial degradation and extractability of different PAH-spiked soils prior and after aging.

MATERIALS AND METHODS
Experiments were accomplished using two different types of soil, a silty loam (8 % organic matter) and a loamy sand soil (0.8% organic matter). Both soils were spiked with a mixture of four PAHs (phenanthrene, anthracene, fluoranthene and pyrene) at a concentration of 2000 mg/kg each. In order to prevent biodegradation during aging soils were sterilized prior contamination using a tyndallisation procedure (100°C for 1 h, 37°C for 24 h; 3 times). Aging was carried out at 4°C in the darkness for 136 days. Aged and non aged spiked soil samples of both soil types were used for extraction, biodegradation and bioluminescence inhibition tests (LUMISTOX using *Vibrio fischeri*, 30 minutes incubation).
A Supercritical Fluid Extraction (SFE) procedure using carbondioxide as extraction fluid was developed earlier for characterization of the extractability of PAHs in soil (LOIBNER et al. 1997): an extraction ratio was calculated by relating the contaminant fraction extracted under 'gentle' SFE conditions to the total concentration of PAHs.
Biodegradation experiments were accomplished in microcosms at 30°C and 90 % humidity for 42 days. Irrigation and mixing of the soil was carried out every second day.

RESULTS AND DISCUSSION
Figure 1 shows the influence of organic matter and aging on the biodegradation of PAHs (total) in soil. Biodegradability is significantly reduced with aging of PAH-spiked soil, whereas this effect is more pronounced with higher organic matter content assuming intensive interaction of PAHs with humic substances (WEISSENFELS et al. 1992,

BRUSSEAU et al. 1991). Only a marginal influence of organic matter on the biodegradability was observed in aged soil (decrease of biodegradation with increase of organic matter). However, in the case of non aged soil the contrary was observed, with biodegradability being increased with higher organic matter content, which may be due to the higher microbial activity (basic and glucose induced respiration, dehydrogenase activity) in the silty loam soil (SCHLEGL, 1996), superimposing the effect of organic matter.

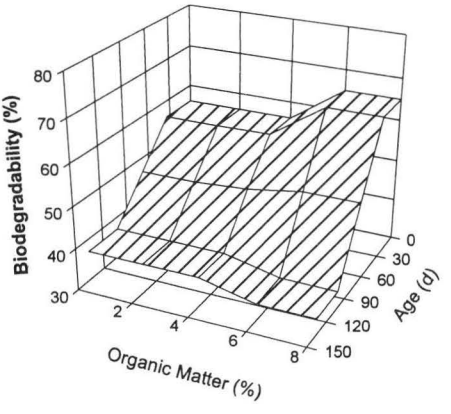


Figure 1: Influence of aging and organic matter content on biodegradability of PAHs in soil.

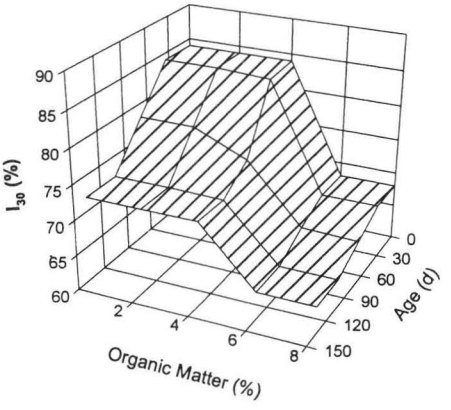


Figure 2: Influence of aging and organic matter content on bioluminescence inhibition of PAH-spiked soil.

Toxicity response (bioluminescence inhibition) is reduced by aging and increasing organic matter content as well (Figure 2), indicating a decline of the leachable fraction of PAHs in soil. It is interesting that while biodegradation increases with organic matter in non-aged soil, toxicity decreases, making e.g. acute toxicity tests of elutriates only, a questionable tool for predicting the progress of bioremediation.

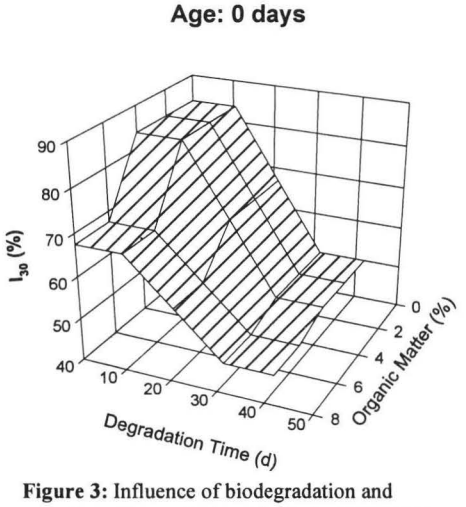


Figure 3: Influence of biodegradation and organic matter content on the bioluminescence inhibition of non-aged PAH-spiked soil.

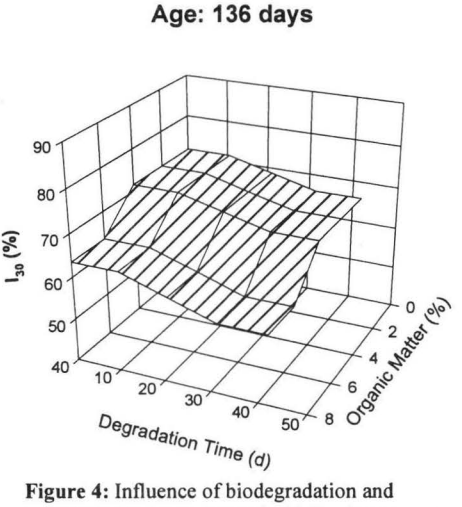


Figure 4: Influence of biodegradation and organic matter content on the bioluminescence inhibition of aged PAH-spiked soil.

In addition toxicity response was monitored during biodegradation of the different PAH-spiked soils (figures 3 and 4). For both, non-aged and aged soil bioluminescence inhibition decreased with increasing degradation time and organic matter content. However, soil aged for 136 days showed significantly less toxicity reduction in the course of bioremediation (figure 4). This phenomenon may be explained with reduced bioavailability (leachability) due to aging at the beginning of the biodegradation experiment and the possible occurrence of toxic, leachable metabolites at the end of the degradation period. Analysis of possible PAH metabolites was beyond the scope of this research programme.

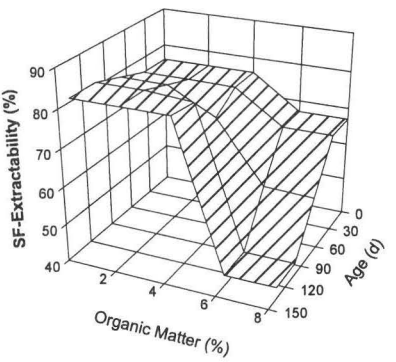


Figure 5: Influence of aging and organic matter content on the supercritical fluid extractability of PAH-spiked soil.

Finally extractability of PAHs in different soils was determined using supercritical carbon dioxide extraction prior and after aging (figure 5). The pattern is very similar to the biodegradability and toxicity studies (figures 1 and 2) with small extractable amounts of total PAHs for aged soil containing high organic matter. The marginal increase of extractability with aging for the low organic matter soil, however, may be the consequence of non-optimum SFE parameters for soils exhibiting low organic content. Nevertheless, SF-extractability may prove to be a powerful tool for predicting toxicity as well as biodegradation success for PAH contaminated soil.

REFERENCES

Brusseau, M. L., Jessup, R.E. and Rao, S.C., (1991) Nonequilibrium Sorption of Organic Chemicals: Elucidation of Rate-Limiting Process, *Environmental Science and Technology* 25, 134-142

Loibner, A.P., Gartner, M., Schlegl, M., Hauzenberger. I. and Braun, R., (1997) PAHs: Rapid estimation of their bioavailability in soil, Battelle press, Columbus/ Ohio, *In-Situ and On-Site Bioremediation*, 4 (5), 617-622

Schlegl, M., (1996) *Extraktion mit superkritischem Kohlendioxid zur Bestimmung des boden- und alterungsbedingten Einflusses auf die Bioverfügbarkeit von polycyclischen aromatischen Kohlenwasserstoffen.* Universität für Bodenkultur, Wien

Weissenfels, W.D., Klewer, H., Langhoff, J. (1992) Adsorption of polycylic aromatic hydrocarbons (PAHs) by soil particles: influence on biodegradability and biotoxicity, *Applied Microbiology and Biotechnology* 36, 689-696.

Site-ASSESS, A DECISION SUPPORT SYSTEM FOR DESIGNING SAMPLING STRATEGIES

Colin C Ferguson[1], Peter Tucker[2] and C Paul Nathanail[1]

[1]CRBE, Nottingham Trent University, Nottingham NG1 4BU, England
[2]University of Paisley, Paisley PA1 2BE, Scotland

Key words: sampling strategies, contaminated sites, software tool, site investigation, statistics, risk assessment.

Pressure to redevelop former industrial land has increased the need for better site investigation tools. An important component of risk assessment is determining the nature, extent and significance of soil contamination. Sufficient information of acceptable quality is required to arrive at robust decisions based on the likely positions of contaminant hotspots and the estimated spatial distribution of contaminants in soil.

Regular sampling designs, which assume that all parts of a site have an equal probability of containing a hotspot, may require large numbers of sampling points. More cost effective sampling strategies can be devised when there are grounds for relaxing the equiprobability assumption and concentrating investigative efforts in areas suspected of being contaminated.

Experienced assessors will often suspect that some parts of a site are more likely to contain a hotspot than others. They may then wish to design a sampling strategy that reflects their degree of suspicion or strength of belief about the hotspot's likely location.

Site-ASSESS (Assessment of Sampling Strategies Expert Support System) is a computer-based decision support system for the design of sampling strategies for contaminated sites. It has been developed as part of the UK Department of the Environment, Transport and the Regions' research programme on assessment and management of contaminated land.

Site-ASSESS is intended to help site investigators design the initial, or first stage, sampling of a site. It develops an optimised sampling pattern for detecting (though not delineating) hotspots, and provides a statistical justification for the chosen strategy.

A compromise between sampling completeness and cost must be achieved, with sampling becoming a statistical exercise to maximise useful information at a cost as low as possible consistent with the objectives of site investigation. When the objective is to locate hotspots, it is sufficient to place just one sampling point on the area covered by a hotspot. Therefore if a circle equal to the radius of the putative hotspot is drawn around a sampling point, the circle can be thought of as the zone of coverage for that sampling point.

The total sampling coverage is the sum of all zones of coverage excluding overlaps. The ratio of the total coverage to the total site area can also be thought of as the probability of hitting a hotspot if it exists. *Site-ASSESS* is developed around this concept of coverage and hit probability. The computational part calculates an optimum sampling design in the light of prior evidence for the existence of a hotspot. Before running *Site-ASSESS* the user

should therefore have already completed a preliminary survey of the site and have compiled:

(i) data on the historic use of the site;
(ii) a record of any visual or other indications of potential contamination gained during a site walkover.

This prior information can be used to calculate a spatially distributed set of *a priori* probabilities that a hotspot exists within specified subareas of the site defined by information grid cells.

The primary motivation for a sampling scheme is to ask: "What is the probability of locating a hotspot *if it exists*?" If, however, the sampling scheme fails to locate a hotspot, the question then becomes: "What is now the probability that a hotspot exists given that the sampling scheme has failed to find one?" This (after the event) probability is termed the *a posteriori* probability. The probability of locating the hotspot, if it exists, can be considered as the hit probability which is equal to the sampling coverage.

A Bayesian probability approach is used to relate the three probabilities:

$$PrH_i = 1 - PrA_i\,(1 - P_i)/(P_i(1 - PrA_i))$$

where PrH_i is the hit probability for grid square i, P_i the *a priori* probability and PrA_i the *a posteriori* probability. By setting one of the sampling objectives (i.e. PrH_i or PrA_i) to a fixed target value, the above equation can be used to compute the other probability.

The hit probabilities for each grid square are then used to calculate the target number of samples for the whole site. The problem is how to distribute the total number of samples over the site such that each grid square requirement is satisfied. This is a well-defined optimisation problem that can be solved using the Quasi-Newton method. However, this is a local optimisation procedure and, in practice, a good initial estimate is essential which is found using an approximate sequential placement algorithm.

Site-ASSESS provides a standardised framework for sampling design. It uses readily available prior information acquired during a desk study and walkover survey. Some practitioners fail to use these data effectively in sampling design (although the data have been collected at some expense) and recourse to a regular grid pattern is the norm for site sampling. The objective should be to find a balance between minimising sample numbers and maintaining acceptable statistical confidence. The system provides a pioneering methodology for helping to achieve that balance.

This work was funded by the UK Department of the Environment, Transport and the Regions, but the views expressed are those of the authors and do not necessarily represent those of the Department.

HOW MANY SAMPLES? BALANCING COST AGAINST RISK IN SAMPLING DESIGN

Colin C. Ferguson
CRBE, Nottingham Trent University
Nottingham, NG1 4BU, U.K.

Key words: sampling theories, risk assessment, cost-benefit analysis, guidelines

If surficial soils were uniformly contaminated at a concentration C, acceptance or rejection of a parcel of land with respect to a human health guideline value G would simply depend on whether C was less than or greater than G. In reality contaminant concentrations will vary across the chosen area and human intakes will reflect that variation. The arithmetic mean concentration will usually be a reasonable guide to contaminant intake so long as the time-averaged exposures to different parts of the area are broadly the same.

In practice it is never possible to know the true mean concentration μ of a contaminant. Decisions have to be made on the basis of an estimate C derived from n sample values c_1, c_2, ..., c_n. It is evident that a large sample size (large n) will generally provide a better estimate of the true mean concentration than a small n. This paper describes how the sample size can be chosen to balance the costs of sampling and analysis against the risk of making one or other of the following errors:

I Wrongly concluding that μ is less than G when in fact it is greater. Because this type of error could put a site user at unacceptable risk, the chance of committing such an error may be called *the occupant's risk.*

II Wrongly concluding that μ is greater than G when in fact it is smaller. This type of error is health protective but could lead to unnecessary and costly remedial action. Alternatively, more detailed sampling and analysis for acceptance testing or remedial design is likely to reveal that μ is probably not greater than G. The site investigator may suffer loss of credibility and even financial liability for the additional costs resulting from the error. This type of error may therefore be called *the investigator's risk.*

The occupant's risk is conventionally denoted by α, which is the significance level of a test used to decide whether μ (which is unknown) exceeds G. The complement, $1 - \alpha$, is called the *confidence level* of the test. The chance of making a type II error (i.e. the investigator's risk) is usually denoted β. Its complement, $1 - \beta$, is called the *power* of a test to detect a difference between the guideline value G and the true mean μ with a sample size of n when the test is carried out at the $1 - \alpha$ level of confidence. Therefore β has no practical meaning unless a particular difference $\Delta = G - \mu$ is specified.

When the true mean value μ is less than the guideline value G, but is not much less, a type II error is not so important. But as the difference between μ and G increases, type II errors will be less tolerable. Thus one can think of a fuzzy zone in which an investigator's tolerance for error is quite high. There are no hard and fast rules for deciding the width of the fuzzy zone but, intuitively, about 30% of the guideline value ($\Delta = 0.3$ G) seems about right.

Contaminated Soil '98, Thomas Telford, London, 1998, 803–804

The standard deviation σ of the underlying contaminant distribution is also unknown. For the purpose of deriving a sample size, it will usually be necessary to make an educated guess (say, half the hypothesised mean value). Therefore, for a hypothesised mean $\mu = G - \Delta = 0.7\ G$, an initial estimate of standard deviation would be $\sigma = 0.7G/2$. Hence the default value of the ratio $d = \Delta/\sigma =$ would be calculated as $d = 0.3/0.35G = 0.857$.

Of course, once samples have been taken and analysed an estimate of σ will be available and the sampling strategy may need to be revised if the initial guess proved to be substantially in error.

Balancing certainty against cost, reasonable choices for the occupant's risk and investigator's risk might be taken as $\alpha = 0.05$ (95% confidence) and $\beta = 0.20$ (80% power). Using the default value of d this would imply a default sample size of about 10 over an appropriate sampling area (Figure 1). Once samples have been taken and analysed, the reasonableness of the initial assumptions can be checked , and more accurate estimates of decision error rates can be calculated.

The simple decision chart (Figure 1) offers a rigorous and robust basis on which to choose a sample size for acceptance testing. When the objectives of sampling are different, other sampling strategies will be appropriate (e.g. Ferguson 1993, UKDOE 1994, Ferguson *et al* 1998).

This work was funded by the UK Department of the Environment, Transport and the Regions but the views expressed are those of the author and do not necessarily represent those of the Department.

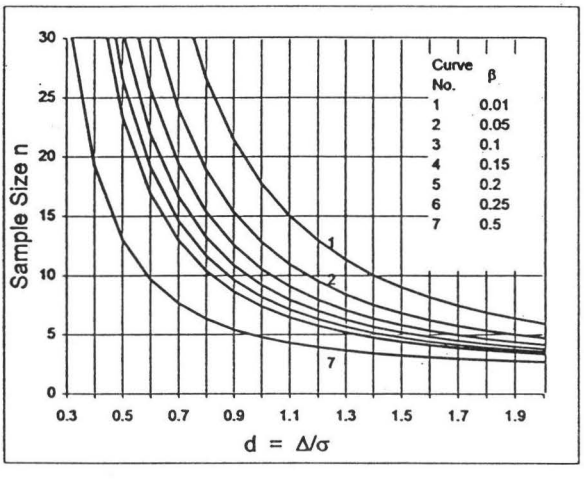


Figure 1 Decision chart for choosing sample size n. For a fixed occupant's risk ($\sigma = 0.05$) the sample size depends on the investigator's risk (β), the difference $\Delta = G - \mu$, and the standard deviation σ of the underlying contaminant distribution.

Ferguson, C. C. (1993) The statistical basis for spatial sampling of contaminated land. *Ground Engineering* 25/5, 34-38.

UKDOE (1994) *Sampling strategies for contaminated land.* Department of the Environment CLR Report No.4.

Ferguson, C. C., Tucker, P. and Nathanail, C. P. (1998) Site-Assess: a decision support system for designing sampling strategies (this volume).

NATURAL BIOLOGICAL TREATMENT OF POLLUTED SEDIMENTS

Joop Harmsen

DLO Winand Staring Centre for integrated Land Soil and Water Research
P.O.Box 125, 6700 AC Wageningen, The Netherlands.

Key word: biodegradation, dredged material, field study, natural attenuation, on-site treatment, PAH, sediments,

INTRODUCTION

A considerable proportion of the pollution in sediments of ditches and water courses in the Netherlands is caused by Polycyclic Aromatic Hydrocarbons (PAHs). These compounds are biodegradable and sediments can be cleaned using common intensive techniques like a bioreactor, but also using a more time consuming method like landfarming. To clean the high amount of polluted sediments cheaper methods are necessary. These methods, using natural occurring processes, are presented.

SPREADING OF SEDIMENTS

In the Netherlands spreading of sediment from ditches over the adjacent agricultural fields was during centuries the normal way of treatment. Because it is found that most sediments are polluted this way of treatment will not be allowed any more in the near future. The natural attenuation and the possibility of accumulation were studied in a real situation on the island of Goeree-Overflakkee. In a part of the study long term degradation and accumulation were compared in sites, not influenced by sediment (reference locations), and banks of the ditches (table 1). Dredging histories of the ditches were known.

TABLE 1. Results of statistical analyses of the comparison of the bank of the ditches with the reference locations. Concentrations are presented as the mean logconcentration (10 log) in mg.kg^{-1} d.m.

PAHs	bank of the ditches mean logconc	Reference locations Mean logconc	statistical analyses	
			Significant increase	Relation accumulation with time
VROM 10	0,40	0,28	Yes	no
EPA 16	0,62	0,48	Yes	no
2+3 rings	0,17	0,11	Yes	no
4 rings	0,38	0,27	Yes	no
5+6 rings	0,15	0,10	Yes	No

Spreading of the sediment is responsible for ⅓ of the load of PAHs and ⅔ is caused by other sources. In the field study to short time degradation it is found that intrinsic degradation is responsible for removal of the PAHs. About 70% are removed within one-and-a-

half year after dredging the ditch. Compared to the higher ring PAHs, the lower ring PAHs are easier removed.

INTENSIVE AND EXTENSIVE LANDFARMING

The way landfarming is used depends on the limiting factor in the specific sediment. With intensive landfarming in the open air it is possible to dewater the sediment to obtain the necessary aerobic circumstances. Tillage or vegetation stimulates the evaporation. Tillage can change a sediment layer of 1 meter into an aerobic soil within in one summer period. The cheaper and natural method with vegetation takes more time, because development of vegetation with roots in the whole layer of sediment takes more than one year. In both cases it is important to remove the surplus of rainfall. During and after the dewatering the bioavailable fraction is removed. If the residual concentration is to high a following extensive treatment (intrinsic landfarming) can be used to reduce the residual concentration. It is found that with a normal agricultural treatment (tillage only once a year) degradation slowly continues. However, several decades can be necessary for complete removal of the contaminant.

LANDFARMING AND LAND USE

In a dense populated country as the Netherlands land must have a function. Using a large surface for an extensive landfarm, without any other beneficial use, will be difficult to accept. For a biological treatment method, growing of vegetation can have a positive effect. Plants create an aerobic and a biological active environment. Therefor landfarming can be combined with growing of vegetation. Although plants do not accumulate PAHs, a consumable product from a 'polluted' site will difficult to sell. Therefor cleaning of soil should be combined with growing of non-consumable vegetation. Possibilities are combination with nature development, but also growing of biomass for energy production. For the latter combination a large-scale investigation is started on some experimental fields. Biomass will be produced using willows. The wood will be burned to produce electricity. Risks for the environment are an important part of the study. In this combination two products are produced, clean soil and energy. Because the production costs are shared, the costs for both products will be lower and can be optimised. This has to result resulting in a cheap biological treatment method for polluted sediments and production of cheap energy.

REFERENCES

J. Harmsen, H.J.J. Wieggers, J.J.H. van de Akker, O.M. van Dijk Hooyer, A. van den Toorn and A.J. Zweers (1997). Intensive and extensive Treatment of dredged sediments on landfarms. In: Papers from the Fourth International In Situ and On-Site Bioremediation Symposium New Orleans, April 28- May 1, 1997. Volume 2, pp. 153-158. Battelle Press, Columbus.

J. Harmsen, J.J.H. van de Akker O.M. van Dijk Hooyer, A. van den Toorn and H.J.J. Wieggers (1997), *Natural attenuation of PAHs in dredged sediments on agricultural fields.* In: Papers from the Fourth International In Situ and On-Site Bioremediation Symposium New Orleans, April 28- May 1, 1997. Volume 2, pp. 143-148. Battelle Press, Columbus.

DIELECTRIC MEASUREMENTS OF CLAY AS A POTENTIAL METHOD OF CONTAMINANT DETECTION

M. Carrier[1], K. Soga[2]
[1] Post Graduate Research Student, Dept. of Engrg., Univ. of Cambridge, Trumpington St, Cambridge, CB2 1PZ, UK
[2] University Lecturer, Dept. of Engrg., Univ. of Cambridge, Trumpington St, Cambridge, CB2 1PZ, UK

Key words: characterisation, clay, contaminated soil, environmental investigations, environmental technology, geoelectrical measurements, geophysical methods, heavy metals, in situ measurement technique, site investigation

SUMMARY

Dielectric properties of materials are a measure of the polarisability of charge carriers in an alternating electric field and are related to their structural and chemical properties. There has been considerable recent interest in the application of dielectric measurements of soil properties to detect the presence of contaminants.

If refined this method has the potential to provide a non-destructive in situ measurement technique which will improve site characterisation and site investigation processes. An experimental programme has been designed to measure the dielectric properties of clays contaminated with inorganic contaminants under controlled laboratory conditions and over a very wide frequency range. The aim of the experimental work is to assess if a change in the type or concentration of inorganic contaminants in clays will be reflected in the dielectric response and if so, at what frequency range.

The dielectric response of an inhomogenous material such as clay contains contributions from several polarisation effects that will be observed at a characteristic relaxation frequency. To usefully characterise such a material, measurements should be taken over a wide frequency range as opposed to at particular frequencies. In order to observe dielectric dispersion in clays due to the polarisation of the diffuse double layer around clay particles, the Maxwell Wagner effect different constituents of the clay-pore water system and water content, observations over a frequency range between 1 Hz and 10 GHz are required.

EQUIPMENT AND METHOD

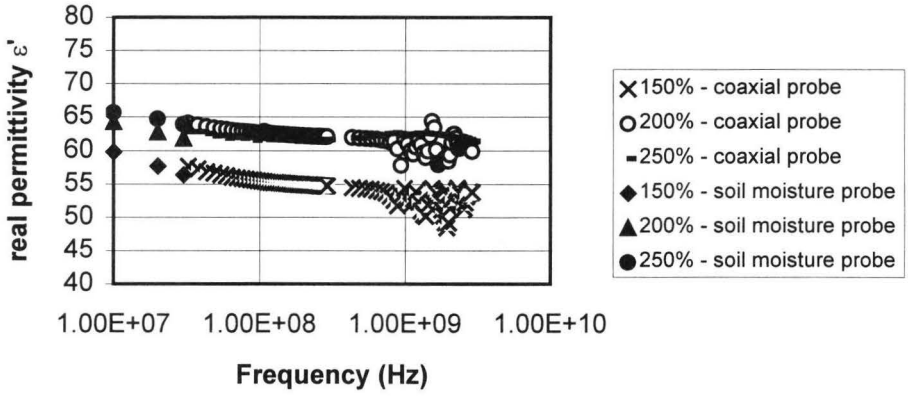
At present, fully transportable and practical in situ dielectric measurement devices are not available. To cover the required frequency range for these experiments three different measurement systems were required. The scope of this study was limited to the use of small, non-destructive, in situ sensors. Measurments of clay-pore water samples are made at different ionic concentrations of the pore water and at different water contents.

For low frequency measurements a four terminal electrode sensor (1 Hz - 10 MHz) was chosen as it is theoretically less susceptible to electrode polarisation effects. This is being used with a Solartron 1260 Impedance Analyser. At higher frequencies an IMAG-DLO soil moisture probe is being employed for measurements at 10, 20 and 30 MHz and a coaxial probe with a Hewlett Packard Network Analyser between 50 MHz and 3 GHz. Permeability measurements are being conducted on clay samples in parallel to provide independent indications of the chemical and physical response of clay to different contaminant regimes.

RESULTS AND DISCUSSION

An example of high frequency permittivity results from a kaolin slurry sample saturated at different water contents with deionised water is shown in the figure below. Even this simple clay-pore-water system is shown to exhibit different dielectric behaviour with differences in water contents.

Real Permittivity: Egrade kaolin and deionised water @ 150%, 200%, 250% moisture content



At low frequencies inductive effects and electrode polarisation were still observed to make significant contributions to the dielectric response. The data is difficult to analyse as the true dielectric properties of the material are masked and the effect is difficult to remove as it depends on the bulk conductivity and inhomogeneity of the mixture. These are thought to be problems introduced by the use of a four electrode system and requires improvements in front end technology used in conjunction with the current impedance analyser model to improve the sensitivity of the measurements.

DEVELOPMENT OF QUALITY MANAGEMENT PLANS FOR TESTING DECONTAMINATION TECHNOLOGIES FOR SOIL AND GROUNDWATER

Joerg Siebert [1], Burkhard Heuel-Fabianek [1], Kai Steffens [1], Peter Dreschmann [1], Annett Weiland-Wascher [2], Ann Kern [3]

[1] ArGe focon-PROBIOTEC, Schillingsstr. 333, D-52355 Dueren, Germany
[2] Umweltbundesamt, Seecktstr. 6 - 10, 13581 Berlin, Germany
[3] U.S. EPA, NRMRL, 26 West Martin Luther King Drive, Cincinnati, OH 45268, USA

Key words: remediation efficiency, clean-up technologies, quality assurance, quality control, quality standards, sampling programme, monitoring procedures

INTRODUCTION

For many years, the United States of America and Germany have successfully cooperated in the broad area of environmental protection. In April 1990 this cooperation was intensified by a bilateral agreement between the United States Environmental Protection Agency (U.S. EPA) and the German Federal Ministry of Education, Science, Research and Technology (BMBF) with a focus on the remediation of contaminated sites. The purpose of the agreement is to improve the understanding of each country's efforts in developing and demonstrating remedial technologies. The bilateral agreement has the following goals:

- facilitate the understanding of each country's approach to the remediation of contaminated sites,
- demonstrate and evaluate innovative remedial technologies
- compare quality management activities relative to the organization, planning, realization and evaluation of technology demonstrations,
- facilitate international technology transfer between both countries.

During phase 1 of the bilateral agreement (1990 to 1996), remedial technologies were tested and evaluated with respect to their removal efficiency. Other objectives, for example remediation costs were also evaluated. Technology evaluations in the U.S. correspond to the Superfund Innovative Technology Evaluation (SITE) demonstrations, while those occurring in Germany correspond to full-scale site remediation activities. For more details concerning the SITE program as well as technology demonstrations, see Heuel-Fabianek et al. (ConSoil, 1998).

The experience of the joint U.S./German demonstrations revealed the necessity of a comprehensive quality system in Germany to assess the efficiency of remedial technologies. This quality system must comprise the preparation, performance and evaluation of demonstrations in order to allow an independent assessment of the tested technology based on data of known quality. This is a major goal of phase 2 of the bilateral agreement (1996 - 1999).

During phase 2, a German standard procedure for the testing of decontamination technologies will be developed. This standard procedure (**De**utscher **T**echnologiestandard **A**ltlasten **D**ekontamination, DETAD) will be applied to SITE program procedures for five technologies in the U.S. and five technologies in Germany. This approach should allow the German side to adapt suitable elements of the SITE program as well as validate both procedures.

GERMAN STANDARD FOR THE EVALUATION OF THE EFFICIENCY OF TREATMENT TECHNOLOGIES

The German standard procedure, DETAD, describes how to plan and perform project specific remedial technology tests in order to acquire data of known quality. Data of known quality allow an independent and verifiable evaluation of technology efficiency. The DETAD may be used as an independent document or a documented procedure as part of a quality system of an organization as depicted in Fig. 1.

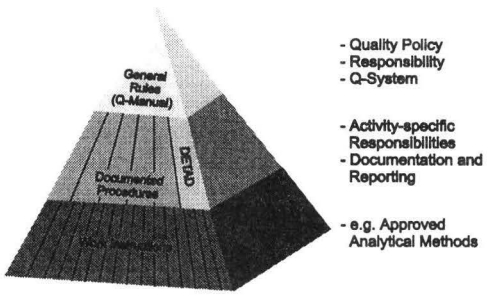


Figure 1: DETAD as part of a quality system

On the basis of test objectives defined by the vendor of the technology, a test plan (QM-Testablaufplan, QM-TAP) will be project specifically prepared describing the strategy of the test. This strategy must ensure that the demonstration, including both field and laboratory activities, yields data of known quality. A test report (QM-Testbericht, TEB) describes both the evaluation of all investigated data during the demonstration, and the assessment of the remedial technology efficiency with respect to the defined test objectives.

The advantage of DETAD is that it provides a standard procedure in Germany for an independent technology evaluation with overall quality management. This procedure produces improved data quality which facilitates and/or optimizes decision processes related to remedial efficiency and cost.

As mentioned above, five technologies will be demonstrated in each country in phase 2 of the bilateral agreement. The currently selected decontamination technologies are:

Remedial Technology	
Germany	**U.S.**
Electron Beam Groundwater Treatment	Enhanced In-Situ Bioremediation
Surfactant Enhanced In-Situ Extraction	Reactive Medium Treatment System
Bioremediation of TNT-contaminated Soil	Electrokinetic Remediation
Soil Vapor Extraction with Catalytic Converter	To Be Determined
Reactive Walls	To Be Determined

PERSPECTIVES

The technology demonstrations will be performed in 1998. The first two technology tests on German sites and the first technology test on a U.S. site (see Table above) will begin the first quarter of this year. The experience and knowledge acquired from these demonstrations will be used for further development of DETAD.

In a second step of this research and development program, the experience in developing the standard procedure DETAD will be used to prepare a concept for a standard procedure for monitoring contaminated sites (**D**eutscher **M**onitoringstandard **A**ltlasten **S**icherung, DEMAS). The major part of this work refers to long-term monitoring in order to evaluate the remedial effects and to protect the environment.

INTRINSIC BIOREMEDIATION IN THE CASE OF A DIESEL OIL CONTAMINATION AT A RAILWAY YARD: INVESTIGATION AND POSSIBLE IMPLEMENTATION.

J.J.M. Staps[1], J. Griffioen[2] and A.P. Kok[3]

[1] Holland Railconsult, P.O. Box 2855, 3500 GW Utrecht, The Netherlands
[2] Netherlands Institute for Applied Geosciences, TNO, P.O. Box 6012, 2600 JA Delft, The Netherlands
[3] Dutch Railways Foundation for Soil Remediation (SBNS), P.O. Box 2809, 3500 GV Utrecht, The Netherlands

Key words: natural attenuation, mineral oil, aromatic hydrocarbons, in-situ bioremediation, microbiological degradation.

INTRODUCTION

A cardinal development in the field of soil clean-up techniques is the use of natural attenuation and the application of extensive clean-up techniques. This can lead to a significant reduction in the cost of soil decontamination. Recent literature, chiefly American, has revealed that intrinsic remediation is taking place at a number of contaminated locations.

Specialists from the Environment Group at Holland Railconsult have investigated the occurrence of intrinsic bioremediation at a diesel oil contamination site located in the NS yard Susteren. The study was undertaken as part of supplementary investigations commissioned by the Dutch Railways Foundation for Soil Remediation. The research results were analysed by the Netherlands TNO Institute for Applied Geosciences. The results are to be taken into account in performing the clean-up study.

In the yard at Susteren, diesel oil contamination had taken place in the past as a result of NS activities in the vicinity of a fuel station. The yard is situated in a water protection area.

The contaminated site in question can be ideal for intrinsic biorestoration, due to:

- the limited depth of groundwater contamination
- the fact that benzene (which is not, by nature, easily degradable) is present in small amounts only
- the feature that the principal contaminants (mineral oil, toluene and xylene) are, by nature, easily degradable.

OBJECT OF THE STUDY

The total project involves several phases between the determination of the extent of the contamination in soil and groundwater and the clean-up study study. This publication focusses on the determination of the site specific potential of intrinsic bioremediation.

METHODS

Findings relating to intrinsic bioremediation were obtained by determining a number of macroparameters in and close to the contamination site. The dissolved components determining the redox status and the carbonate chemistry of the groundwater (Fe, Mn,

NO_3, O_2, SO_4, CH_4 and Ca, Fe, HCO_3 and pH respectively) are of chief importance here. These parameters were established not only within the contaminated area, but also downstream and upstream of the contaminated site. The latter can serve as a background reference, providing a record of the natural composition.

RESULTS OF THE MACROPARAMETRIC STUDY

The monitoring wells that were sampled to provide a picture of the underlying composition revealed groundwater that was rich in sulphate and iron. Nitrate and oxygen were below the detection limit and HCO_3 concentration was low.
The monitoring wells in the contaminated area all revealed groundwater without nitrate and oxygen. The presence of methane in the groundwater was apparent, with concentrations of up to 18 mg/l. Iron and HCO_3 concentrations also ranged from high to very high. The sulphate concentrations were relatively low in the area contaminated with diesel oil. The higher anaerobic status of the groundwater inside the contaminated area is a clear indication of the intrinsic bioremediation of organic compounds. This suggests the degradation of, above all, aromatic compounds, since these are in principle degradable in all redox conditions.
At this site an increase in pH from 5 - 5.5 to 6.5 can further be noted at the two upstream wells in the direction of the wells in the contaminated area. This can also be seen as an indication of the occurrence of intrinsic bioremediation.
The groundwater in the monitoring wells downstream from the contamination was characterised as anaerobic with a good deal of iron, a little methane, quite large amounts of sulphate and a moderate quantity of HCO_3. The composition can indeed be considered as originating at the edge of a contamination area where intrinsic attenuation is taking place.
The groundwater from the contamination diffusion area is characterised as groundwater containing no organic contaminants, but revealing redox-sensitive components in solution which are a direct indication of intrinsic attenuation.

CONCLUSIONS

On the basis of the results of this study, it can be concluded that the real risk of the migration of contaminants is considerably smaller than the prevalent notion of the risk of it spreading as determined by urgency systematics would have it: intrinsic attenuation of mono-aromatics is an additional mechanism limiting the migration of contaminants as a whole. The real risk of contamination spreading is probably strongly dependent on the diffusion of the mineral oil in the groundwater. For mineral oil, intrinsic bioremediation is only possible from the edges of the contamination area if the non-contaminated groundwater contains oxygen or is oxic. This is not considered impossible at this location. Furthermore, sorption and dispersion are two mechanisms that lead to an intrinsic reduction in groundwater contamination.
Since intrinsic bioremediation has been indicated, this aspect is to be taken into special account in the next phase of the work, a study comparing applicable clean-up methods. Because the location is in a groundwater protection area, special attention will be paid to monitoring and minimising the risk of diffusion.
The poster contains further details of the processes of intrinsic bioremediation and on the remit for the follow-up phases comprising the clean-up study (comparing applicable clean-up methods) and plan.

Purification of Contaminated Particulate Material through Chemical Conversion

Bernhard Peters
Research Centre Karlsruhe, P.O. Box 3640
D-76021 Karlsruhe, Germany

Keywords: chemical treatment, contaminated soil, decontamination techniques,mathematical models, porous media, simulation model, thermal treatment

Large quantities of contaminated particulate material such as soil stem from industrial residuals often thoughtlessly exposed to the environment. A less frequent source of contamination is represented by accidents, discharging hazardous gas or liquids into the environment in an uncontrolled manner. In addition, the processing industry is constantly dealing with aged catalytic pellets from processes such as reforming where material has to be regenerated after a certain period.

A treatment often used for contaminated material consists in exposing it to high temperatures during perhaps a combustion process or in maintaining a chemical conversion process by addition of some predefined reactants. In order to achieve sufficient regeneration or decontamination, the ambient conditions of the process, such as temperature or availability of reactants, need to be adjusted. Furthermore, the residence necessary time to achieve a given degree of conversion has to be determined. Experiments are difficult due to limited access and thus are expensive. The objective of this study is to present a numerical method to calculate the temperature evolution and the conversion rates for a contaminated particulate material. The main novelty of the method is that it can be applied to particles of different sizes, composition and degrees of contamination. It is a cost-effective method which allows to obtain estimations rapidly even if parameters of the scenario are subject to change.

The method chosen for the purification of particles through chemical conversion is based on the one-dimensional and transient conservation equations for species and energy. The assumption of one-dimensionality is also supported by Man [1] who detected mainly one dimensional behaviour in a comparison of his results with experimental data. The conservation equations are written in a differential form for particles considered spherical. This assumption is valid, since the effectiveness factor, which represents a measure for the reaction progress in porous particles, does not vary significantly for different particle shapes ranging from cylindrical to flat particles. Further evidence of this behaviour is provided by the experimental investigations of Senf [2]. His results indicate that the PM emissions and volume to surface ratios are not correlated. Heat and mass transfer from the ambient gas phase is taken into account. The set of coupled equations is solved by a time marching finite volume method with appropriate boundary and initial conditions. The solution yields the evolution of inner particle variables such as temperature, concentration and degree of decontamination in time and space.

Contaminated Soil '98, Thomas Telford, London, 1998, 813–814

The capabilities of the method are demonstrated by the two limiting cases with high and low Thiele modules representing the shrinking core model and the reacting core model for a single particle shown in figure 1

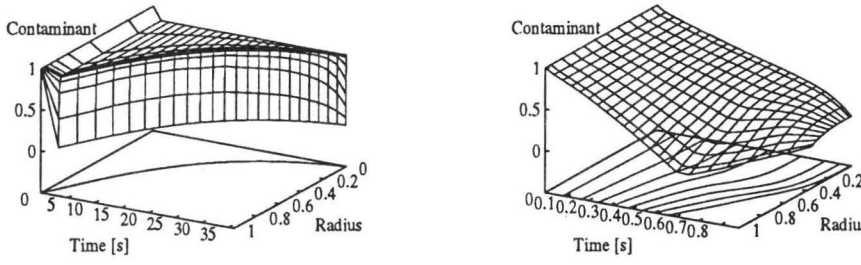


Figure 1: Distribution of the contaminant for different conversion modes

The purification process is to a large extent determined by the gaseous reaction partner available on the exterior surface and in the interior of the particle. The inner distribution of the gas depends on the ratio of transport to reaction that lets the reactant penetrate to the centre of a particle. For the case of limited penetration i.e. for a high Thiele module, shown in the left part of figure 1, the gaseous reaction partners initially available are depleted within a short period. The reaction within the particle is limited only to a thin layer with steep gradients, in which both the reactants and the contaminant are depleted. This behaviour prevents gaseous reaction partners from reaching interior parts of the particle where the concentration is close to zero.

Different profiles are encountered for the case for which the gaseous reaction partner is able to access easily the interior of a particle. Hence, only minor differences versus radius appear for all relevant variables as shown in the right part of figure 1. The levels of gaseous species decrease continuously as the reaction rate increases with higher temperature.

In conclusion, the method presented is suitable to calculate the chemical purification process of a contaminated particle versus time and radius. Since the transient transport phenomena are described by the appropriate differential equations, the method covers the entire range between the reacting core and the shrinking core regimes. Hence, the quality of a decontamination process based on chemical conversion can be evaluated taking the most important parameters of the process into account.

References

[1] Man Y. H. and Byeong R. C. A numerical study on the combustion of a single carbon particle entrained in a steady flow. *Combustion and Flame*, 97:1–16, 1994.

[2] Senf N. Low emissions residential cordwood combustion in high mass appliances - recent research and results. In *Combustion Canada '96, Ottawa, Ontario, Canada*, June 5 - 7, 1996.

GROUNDWATER RISK ASSESSMENT AT A CONTAMINATED SITE BASED ON INTEGRATING AND SPATIALLY RESOLVING INVESTIGATIONS OF GROUNDWATER POLLUTANT CONCENTRATIONS AND FLUXES

T. Ptak, R. Schwarz and G. Teutsch

University of Tuebingen, Applied Geology, Sigwartstr. 10, D-72076 Tuebingen, Germany (e-mail: thomas.ptak@uni-tuebingen.de)

Key words: Contaminated sites, site investigation, groundwater, groundwater monitoring, contaminated plume, risk assessment, computer model, data analysis.

SUMMARY
A new investigation method for the assessment of groundwater contaminations was applied at an abandoned landfill site. Based on a spatially integrating measurement approach, the application of the method yields the contaminant concentration distribution as well as the total mass flux over a control plane within a contaminant plume. The investigation method is described and some results from its first application are presented.

1. INTRODUCTION

At many contaminated sites the presence of pollutant hot spots as well as preferential transport paths and low conductivity zones within the aquifer result in an irregular distribution of contaminants in groundwater. Under such conditions, many costly monitoring wells would be needed to reliably determine the concentration distribution downstream of the pollutant source. Therefore, a new investigation method for groundwater risk assessments is proposed (Teutsch et al., 1998). The method is based on a spatially integrating measurement approach in order to consider the influence of the entire contaminated site, without the need to regionalize point scale concentration measurements.

2. INVESTIGATION METHOD

In the new investigation method one or more groundwater pumping wells are placed and operated simultaneously or sequentially downstream of a pollutant source, with positions, pumping rates and pumping times allowing the well capture zones to cover the overall width of the contaminant plume. During pumping, the depth integrated concentration of one or more groundwater contaminants is measured as a function of time at each of the pumping wells.

For the interpretation of the concentration time series measured at the pumping wells, an inversion approach and a computer program were developed (Schwarz et al., 1997). Using the numerical inversion technique it is possible to calculate the spatially variable contaminant concentration distribution over a control plane perpendicular to the groundwater flow direction undisturbed by pumping, as well as the mass flux over this control plane. The mass flux obtained is representative of the whole contaminated site. The computer program allows a non-stationary evaluation of concentration time series measured at different pumping wells within a non-uniform three-dimensional groundwater flow field, and it takes into account the spatial variability of aquifer parameters.

3. APPLICATION OF THE NEW INVESTIGATION METHOD

The new investigation method was first applied at an abandoned landfill site near Heidelberg in the Rhine Valley in Germany. At this site the groundwater within the porous aquifer of 15 m thickness is contaminated with chlorinated hydrocarbons (TCE and PCE). A total of six pumping wells, each with a pumping rate of 3.0 l/s, were positioned along a control plane of 180 m length. The wells were operated in two consecutive campaigns (each one with

three active wells) to cover the whole contaminant plume downstream of the landfill. Each of the two pumping campaigns had a duration of 14 days. Groundwater pollutant concentrations were measured at each of the pumping wells with sampling intervalls allowing a spatial resolution of about 0.5 m along the control plane. Within the first campaign, 45 measurements were taken at each of the wells, and 53 within the second.

Following the measurements, the concentration time series were evaluated using the numerical inversion technique and a local scale flow and transport model. As an example of the results, Figure 1 shows the distribution of depth averaged concentrations of TCE along the control plane downstream of the landfill.

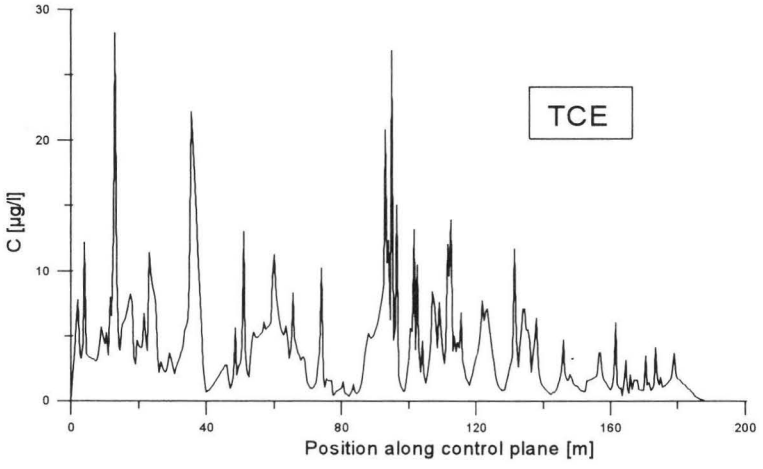


Figure 1. Distribution of depth averaged TCE concentrations along the control plane.

The average TCE concentration is 6.0 µg/l, and the total TCE flux is 2.51 g/d. Both values are representative of the whole contaminant plume downstream of the landfill.

4. DISCUSSION AND SUMMARY

It follows from the spatially variable TCE concentration values shown in Figure 1, that the conventional site assessment approach based on interpolation of concentrations obtained from local scale measurements bears the risk of under- or overestimation of the groundwater contamination, depending on where the monitoring wells were positioned. In comparison, the new investigation method, based on an inversion of concentration time series measured at pumping wells, offers a 100 % coverage of the contaminant plume, without the need for a costly monitoring network. Therefore it allows a quick and accurate estimation of the average contaminant concentration, of the concentration distribution along a control plane as well as of the total contaminant mass flux downstream of a contaminant source.

REFERENCES

Teutsch, G., Ptak, T. and Holder, T. (1998) Eine neue Methode zur Bestimmung der Immission an kontaminierten Standorten, to be published in *Grundwasser*.

Schwarz, R., Ptak, T. and Teutsch, G. (1997) *Grundwasser-Gefährdungsabschätzung durch Emissions- und Immissionsmessungen an Deponien und Altlasten: Numerische Untersuchungen zur Anwendung und Auswertung*, Bericht, PWAB Baden-Württemberg, Projekt-Nr. PD 96 181, Lehrstuhl für Angewandte Geologie, Universität Tübingen, Germany.

EVALUATION OF HEAVY METAL MOBILITY THROUGH THE UNSATURATED ZONE OF SOIL

I. Le Hécho[1], S. Cornu[1], P. Charbonnier[2], P.Baranger[1], S.Altmann[1]
[1]BRGM, DR, 3 avenue Claude Guillemin, B.P. 6009, F-45 060 ORLEANS Cédex
[2]BRGM, CT DEFIS, Fort de Lezennes, F-59260 LEZENNES

Key words : pollutant transport, mobility, heavy metals, unsaturated zone, soil

SUMMARY

The aim of this study was to understand and to model the transfer of metal pollutants (Cd, Pb, Zn) through the unsaturated zone of the soil towards the groundwater. This transfer is a function (i) of water circulation paths and (ii) of reactivity of pollutants onto the solid phases. The unsaturated zone was divided into isotropic and homogeneous geochemical reactors. The study consisted in (i) establishing the hydrodynamic characteristics of these reactors, using *in situ* measurements, (ii) determining distribution coefficient (Rd) of Cd, Zn and Pb using batch experiments. These data will be incorporated into a coupled chemistry/transport model. Such a model will then be validated using data collected into field experiments. We choose to present mainly in this paper the results concerning the reactivity of pollutants onto the various soil horizons of the studied area.

RESUME

Le programme présenté ici vise à la compréhension et à l'évaluation du transfert de polluants métalliques (Cd, Pb, Zn) vers la nappe souterraine sous-jacente au travers de la zone non saturée du sol. Ce transfert est fonction à la fois des voies de circulation et de la réactivité des polluants par rapport aux phases solides. La zone non saturée a été subdivisée en réacteurs géochimiques isotropes et homogènes. Les étapes ont consisté d'une part à établir les caractéristiques hydrodynamiques de ces réacteurs, à partir de mesures *in situ,* puis, d'autre part, à déterminer expérimentalement les coefficients de partage liquide/solide (Rd). Ces données permettront de construire un modèle couplé chimie/transport adapté au site étudié et qui sera validé à l'aide de mesures réalisées in situ. Nous avons choisi d'axer ce papier sur les résultats concernant la réactivité des polluants par rapport à l'ensemble des horizons de sol prélevés sur site.

Contaminated Soil '98, Thomas Telford, London, 1998, 817–818

This study took place in the North of France, in the "Nord Pas de Calais" region, near Douai. In this region a large industrial and mining activity used to take place. The soils of this sector, developed on sedimentary calcareous deposit, are strongly polluted by Zn, Cd and Pb mainly. These elements are brought to the soil as ashes and slag due to a metal work in their neighbouring. The purpose of this study was to evaluate the movement of metallic Cd, Zn and Pb through the unsaturated zone of a soil towards the aquifer.
Six soil samples were chosen at different depths and were accurately characterised (acid-base titration, CEC, BET surfaces, chemical, mineralogical and granulometric composition, initial concentrations of Cd, Pb and Zn adsorbed). The distribution coefficients were measured using batch experiments. Influence of pH, the total metal and Ca concentrations was studied.
Samples can be divided into 3 distinct groups : (1) a sandy sample containing about 70 % of SiO2 minerals ; (2) 3 clayey to loamy samples containing about 40-50% quartz and calcite free ; (3) 2 calcite rich samples (about 10%), poor in quartz (about 10%). CEC and BET surfaces increased from group 1 to group 3 due to differences of granulometry and mineralogical composition. The buffer capacity sequence is in agreement with the calcite content of the different soil horizons : group 3 >> 1 >> 2.
For high buffer capacity samples (groups 1 and 3), the batch experiment were only realised for natural pH values (around 8). Thus pH influence was only considered for samples of group 2. For these samples, adsorption classically decreases with pH. In the rest of this paper, all the results presented correspond to natural pH values.
Generally, the distribution coefficients decrease when the total metal concentration increases, which indicates classically a beginning of saturation of the adsorption sites of metal onto the solid. Because of the original concentration in metal in the studied samples and of the detection limit of the studied methods, we were obliged to use high metal concentrations in the batch experiments. We were thus unable to determine the true distribution coefficient (Kd) of the studied samples.
Influence of Ca concentration on metal adsorption changed according to the different group of samples. An increase of Ca concentration did not influence adsorption onto the calcite rich samples (group 3) but strongly decreased adsorption onto the sandy sample (group 2). As Ca concentration increased, Pb adsorption onto the samples of group 2 decreased while Zn adsorption onto these samples did not vary a lot (adsorption of Cd was not studied for different Ca concentrations for these samples). These different behaviour can be explained by mineralogical differences among samples. Calcite rich samples lead to high Ca concentration in the aqueous phase so that the induced Ca variation within the experiment is negligible.

Metal adsorption sequences for the different sample group is : group 1 > 2 > 3. This sequence is the reverse sequence of the CEC and the BET surface one. This result indicates that sorption mechanisms are not directly controlled by cation exchange processes. On calcite rich samples the sorption can be related to metal coprecipitation processes leading to solid solution systems.
On these samples the observed sequence of metal adsorption Pb > Zn > Cd is in agreement with this sorption mechanism.

The next stage of the program will consist to couple water transfer through the unsaturated zone with the water/solid chemical interactions. The resulting model will then be validated using data collected into field experiments.

NATURAL ATTENUATION OF IRON-COMPLEXED CYANIDES IN SOIL AND GROUNDWATER AT FORMER GASWORK SITES

H. Hommelgaard, S.K. Munch, H. Mosbæk and P. Kjeldsen
Department of Environmental Science & Engineering,
Technical University of Denmark, Building 115, DK-2800 Lyngby, Denmark

Key words: Natural attenuation, cyanide, gasworks, soil, groundwater

INTRODUCTION

The process of degassing coal in order to produce city gas initially generated a raw gas containing hydrogen cyanide, which was removed by iron oxides. The spent iron oxides contained large concentrations of iron-complexed cyanides such as Prussian Blue ($Fe_4(Fe(CN)_6)_3$). The iron-complexed cyanides can be leached out especially at high pH-values, thereby entering soil layers and groundwater beneath the spent iron oxide waste. Cyanide in free form has in many studies shown to be easily degradable, however degradation of iron-complexed cyanides has only been studied by very few, and not under conditions relevant to groundwater environments. The objectives of this study was to investigate the natural degradation of iron-complexed cyanides in aerobic microcosms simulating soil and groundwater environments.

MATERIAL & METHODS

The laboratory microcosms were 2 litres containing a suspension of fines from a soil slightly contaminated with iron-complexed cyanides. The soils were taken from two different gaswork sites. Iron-complexed cyanides in the form of potassium hexacyanoferrate ($K_4Fe(CN_6)$ including a small proportion as ^{14}C-labeled hexacyanoferrate ($K_4Fe(^{14}CN_6)$ were added to the batches. Control experiments were carried out where sodium azide was added to inhibit microbial activity. The batches were aerated daily, and the off gas was treated in sodium hydroxide containing traps in order to collect any CO_2 leaving the batches. The experiment were run for a period of 82 days. Water samples were taken several times under the experimental period. After the termination of the experiment the water and the soil in the batches, and the content of the traps were sampled, and mass balances of iron-complexed cyanides, free cyanides, carbon dioxides (all in both labelled and non-labelled forms) and nitrogen containing compounds (NO_3^- and NH_4^+/NH_3) were set up. In total 10 different batches were set up, combining different initial cyanide concentrations, cyanide form, soil, and temperature. Table 1 shows the experimental conditions in the 10 batches.

RESULTS & DISCUSSION

By measurement of the contained $^{14}CO_2$ in the batches and traps after the termination of the experiments, the total amount of hexacyanoferrate mineralised can be calculated using the proportion of initial labelled hexacyanoferrate to the total hexacyanoferrate added. The amount of mineralised hexacyanoferrate after the 82 days incubation as percentage of the added hexacyanoferrate is shown in Figure 1 for all ten batches. The figure shows that between 1 and 18 % of the initial hexacyanoferrate was degraded to carbon dioxide, and that the degradation took place even in the control batches where high concentrations of azide

was added. This could be due to an abiotic degradation process or a degradation by micro-organisms not sensitive to azide. The largest degradation took place in batch 6 where $(Fe(III)(CN)_6^{3-}$ was used instead of $(Fe(II)(CN)_6^{4-})$. For the duplicate batches (batch 1 and 2) equal hexacyanoferrate degradation were observed.

Table 1. Experimental conditions for the ten batches.

Batch no.	1	2	3	4	5	6	7	8	9	10
Soil[a)]	H	H	H	Ø	Ø	H	H	Ø	H	Ø
1000mg CN^- as $K_4Fe(CN)_6$ added	+	+	+	+	+				+	+
200mg CN^- as $K_4Fe(CN)_6$ added							+	+		
1000mg CN^- as $K_3Fe(CN)_6$ added						+				
Azide added (4 g NaN_3)			+		+					
Temperature: 20°C	+	+	+	+	+	+	+	+		
Temperature: 10°C									+	+
135 kBq as $K_4Fe(^{14}CN)_6$ added	+	+	+	+	+	+	+	+	+	+

a) H: Holte Gaswork site Ø: Østre Gasworks site

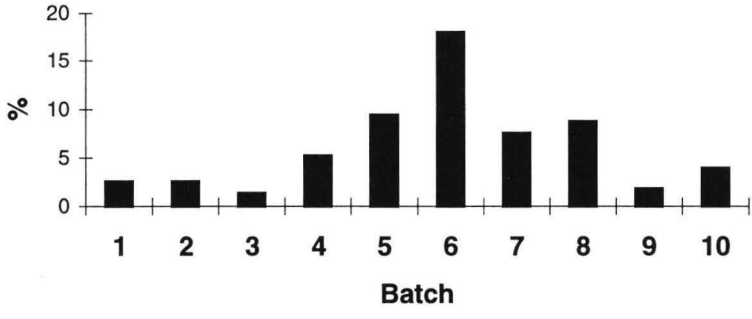


Figure 1. Degraded hexacyanoferrate in percentage of the initial content in the batches.

Also the N-containing components produced by the mineralization of hexacyanoferrate were analysed. For the batches with no azide added the nitrogen was mainly present as nitrate, only a minor part was present as ammonium. In the batches with azide added all nitrogen was present as ammonium. This indicates that ammonium is produced while hexacyanoferrate is degraded, and that the ammonium is nitrified in the live batches. In the batches with final pH-values below 7.7 the molar concentration of carbon dioxide was as expected equal to the molar concentration of nitrate plus ammonium. For the batches containing soil from Østre Gaswork site the final pH was above 8.2. In these batches much lower nitrogen concentrations were found probably due to volatilisation of ammonia to the off gas.

CONCLUSION

The experiments showed that iron-complexed cyanide leached out from spent iron oxides at former gasworks sites may be naturally attenuated in soil layers or aquifers below, due to degradation processes. If oxygen is present the degradation products are carbon dioxide and nitrate.

RISK ASSESSMENT OF PAH IN SOIL: BEHAVIOUR AND FATE OF NON-EXTRACTABLE ^{14}C-PAH-RESIDUES UNDER ENVIRONMENTAL STRESS CONDITIONS

A. Eschenbach[1], R. Wienberg[2], B. Mahro[1]

[1] Inst. für Technischen Umweltschutz, Hochschule Bremen, Neustadtswall 30 28199 Bremen , FRG
[2] Umwelttechnisches Büro und Labor Dr. R. Wienberg, Gotenstraße 4, 20079 Hamburg, FRG

Keywords: behaviour of contaminants, bioremediation, contaminated soil, humic substances, immobilization, isotope methods, PAH, risk assessment

Introduction:
Based on the finding that polycyclic aromatic hydrocarbons (PAH) may undergo a biogenic formation of non-extractable residues in soil it had been proposed to use that process intentionally for bioremediation purposes (Mahro et al. 1996). For this reason it is of interest to determine processes which influence the formation of non-extractable residues (humification) (Eschenbach 1995). However, the intentional use of PAH-humification for bioremediation purposes requires also a careful assessment of the fate and long-time stability of the formed non-extractable PAH-residues. It must therefore be evaluated whether and in which time frame non-extractable residues will remain stable within the soil. A mineralization to CO_2 would be a complete detoxification. A critical point however would be the release of up to that point non-extractable residues as PAH or rather as their metabolites, since this would require to consider the possible risks of the humification-treatment in more detail.
The fate of four different non-extractable ^{14}C-PAH-soil residues, namely ^{14}C-naphthalene, ^{14}C-anthracene, ^{14}C-pyrene and ^{14}C-benzo(a)pyrene, was monitored under different ecological stress conditions by measuring the relative fractions of the evolution of $^{14}CO_2$, the release of extractable ^{14}C-compounds and the non-extractable residual ^{14}C-fraction in the soil.
The experimental concept included both, biological (e.g. effect of PAH-degrading microorganisms, of humus-decomposing pure cultures and organic supplements like compost) and physical-chemical treatments (e.g. influence of freezing and thawing, of mechanical disruption of soil aggregates or complexing agents).

Results:
It was found that those non-extractable residues that had been released from the humic polymer without soil treatment were predominantly mineralized to $^{14}CO_2$ by soil microorganisms. The addition of organic supplements, PAH-metabolizing bacteria and fungi or humus degrading microorganisms did not enhance the mineralization rate. The amount of $^{14}CO_2$ being released from humic bound PAH was comparable with the natural

turnover rate of humic substances. The non-extractable residues were not converted to an extractable form.

The mechanical disruption of the soil structure by ultrasonics was able to increase the bioavailability of the substances to some extent (i.e. the water extractable ^{14}C-fraction) but did not reduce the amount of the non-extractable PAH-residues. Mechanical treaments seem also be able to increase the bioavailability of the xenobiotics and therefore might be used as a pretreatment for soil samples containing compounds with a minor bioavalibility.

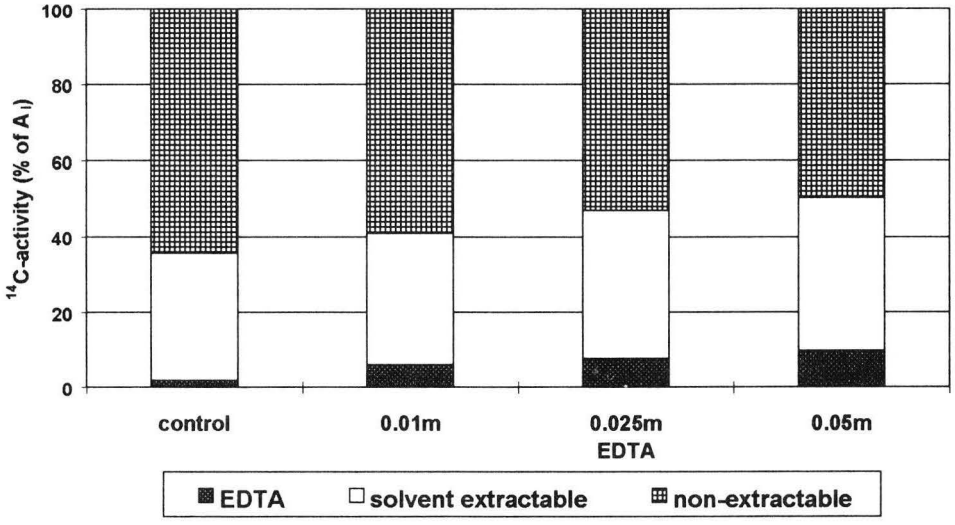


Figure 1: Release of non-extractable ^{14}C-pyrene-residues after resolving metal-organic complexes by an extraction with EDTA-solution in different concentrations

A significant release of non-extractable PAH-residues was detected when complexing agents like EDTA had been added to the soil, as shown in Figure 1. The amount of non-extractable ^{14}C-residues decreased about 15%-points of the initial ^{14}C-activity (A_i). The EDTA-solution (0.05m) was able to extract about 10%-points of A_i. Precipitation experiments with concentrated acids indicate that the disruption of metal-organic complexes led obiously to the release of ^{14}C-activity that had been attached before to colloidal or dissolved organic matter.

References:

Eschenbach, A. (1995): Einfluß von *Pleurotus ostreatus*, Kompost, *Sphingomonas paucimobilis* und der Kontaminationsdauer auf den Verbleib und Abbau ^{14}C-markierter polyzyklischer aromatischer Kohlenwasserstoffe (PAK) in Altlastböden. Ph.d. Thesis Technische Universität Hamburg-Harburg, 215 p.

Mahro, B., Eschenbach, A., Kästner, M. and Schaefer, G. (1996) Possibilities and limitations for the microbial degradation of polycyclic aromatic hydrocarbons (PAH) in soil, in OECD (ed) Wider application and diffusion of bioremediation technologies. The Amsterdam '95 Workshop. OECD Paris, p. 297-307

WATCO REMEDIATION SERVICES
Consulting Bureau Scarabee
Grondreiniging en grondwaterzuivering
assainissement des sols et des eaux souterraines
Remediation of contaminated soil and groundwater

The Ghent soil and waste treatment centre

Watco Remediation Services,
Vilvoordse Steenweg 218,
1120 Brussels, Belgium.
Ir. Jan Haemers

Consulting Bureau Scarabee,
Couwenhoven 62-31,
3703 HN Zeist, The Netherlands.
Ir. Jaap van Hasselt

Keywords: clean-up cost; clean-up technologies; plants.

1 Introduction

Watco Remediation Services (WRS) is a fully owned subsidiary of the Belgian Tractebel group which is planning to build a full scale waste treatment centre in the area of Ghent, Belgium. Consulting Bureau Scarabee assists WRS in the engineering of the innovative concept of thermal treatment of contaminated soils.
In the Ghent waste treatment centre a number of different waste streams are processed, and processes are combined in an innovative way.

In the centre the following waste streams will be processed:
- 200.000 tons/yr. of Municipal Solid Waste (MSW) by means of incineration,
- 175.000 tons/year of contaminated soil by means of thermal treatment,
- Green waste (GFT) by means of composting.
- Sewage sludge,
- Incinerator ashes,
- Cars,
- Electronic waste.

In the centre, the incineration of Municipal Solid Waste and the thermal treatment of contaminated soils will be combined.
Normally, a thermal soil treatment system consists of two process steps:
- the drying and thermal desorption of the contaminants from the soil, and
- a subsequent flue gas treatment system in which the contaminants are destroyed in an incinerator and the resulting flue gases are cleaned to meet emission standards.

Thermal treatment consumes much energy. The energy cost is very often an important part of the total cost of thermal soil treatment.
In the Ghent concept the incineration of MSW is combined with the incineration of the contaminants. The flue gas cleaning system of the MSW incinerator is used to clean the gases of both systems.

Contaminated Soil '98, Thomas Telford, London, 1998, 823–824

2 The soil cleaning unit

A short description of each of the components of the soil cleaning plant is given below:

2.1. Feed preparation

Prior to feeding, the soil is screened to remove particles > 80 mm.

2.2. Drying

A part of the steam, generated in the offgas boiler of the municipal solid waste treatment facility is used to heat the dryer of the soil-cleaning unit. The soil is dried indirectly. A detailed study on the heat transfer rate in an indirect dryer was made.

2.3. Desorption

The desorption unit is a direct fired rotary kiln. Direct desorption offers more flexibility and higher capacity then indirect desorption, a possibility that was also studied.

2.4. Soil cooling

The soil is cooled in a cooler in which water is directly injected

2.5. Flue gas treatment

2.5.1. Treatment of dryer offgas

The dryer offgas, containing evaporated water and light pollutants are cooled in a condenser. The water is cleaned in a water treatment plant.

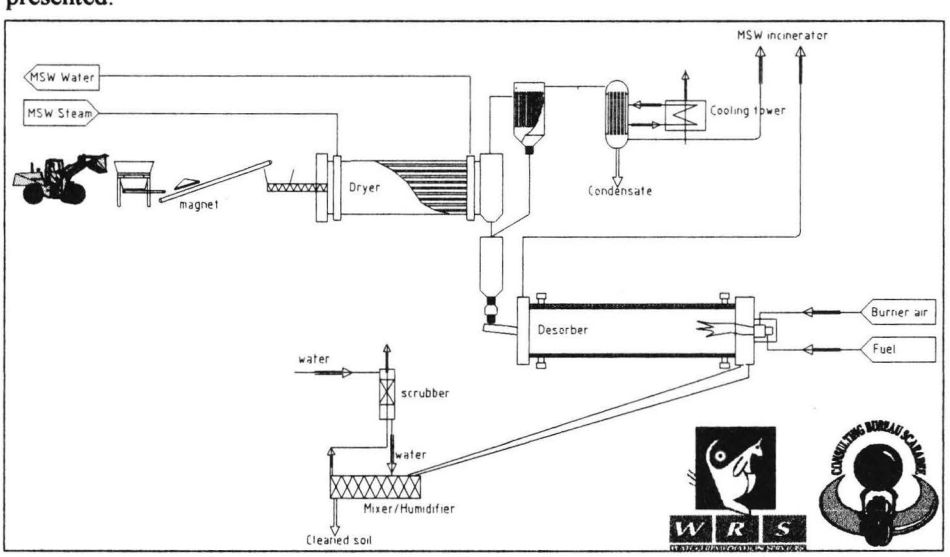
2.5.2. Incineration

The offgases of the desorber of the soil cleaning system are incinerated in the furnace of the municipal solid waste treatment system. The temperature and residence times in the furnace are adequate to destroy all contaminants.

2.5.3. Flue gas cleaning

The remaining rest contaminants are captured in the flue gas cleaning system of the municipal solid waste incineration system.

As a result of this new combination of waste treatment technologies, much energy can be saved, and the cost price for thermal soil cleaning stays at an acceptable level.
At the time of the conference, the engineering of the plants and the permitting phase will be completed; and details of the concept, the engineering and permitting obstacles will be presented.



CHARACTERISTICS OF SOILS POLLUTED BY PAH

P. Barbé[1], P. Lecomte[1] and R. Pazdej[2]

[1] CNRSSP - 930, Boulevard Lahure, BP 537 - 59505 Douai Cedex - France
[2] LECES Environnement - Voie Romaine, BP 40223 - 57282 Maizières-les-Metz Cedex -France

Key words : behaviour of contaminants, contaminated soil, characterization, organic contaminants, PAH (polycyclic aromatic hydrocarbon), migration, clay

Soil characterization of old gas and coke plants polluted by PAH is crucial for their rehabilitation and can give significant information about the mobility of these pollutants. The PAH spectra from an old coke plant have been determined in the subsurface and the aquifer (soil matrix) in the area of the tar deposits.
The geological profile of the old site is made up of sand and clay (6 m thick) toping an aquifer of chalk (50 m thick). The groundwater table is reached between 25 and 30 m from the surface.
Many soil investigations have been conducted during a large period (1990-1995) : a drilling down to 50 m, 94 auger drillings down to 6 m to determine the level of the pollution on the site and 32 close auger drillings reaching the chalk material in the area of a tar deposit. The bottom soil of the old tar pool has also been analysed as regards to the PAH concentrations. During the whole investigation period, all the PAH analyses have been performed in the same laboratory.

The PAH spectra have been set up in the soil of the drilling down to 50 m, giving information about the vertical migration of such pollutants. In this area, the total amount of PAH ranges 1-30 $mg.kg^{-1}$ of dry soil. This spectrum analysis has been focused on the vadose zone (sand and clay, chalk) and on the aquifer (chalk), taking into account the geological specificity :

✓ In the unsaturated zone down to 6 m depth (sand and clay), the PAH spectrum reveals four peaks: phenanthrene, fluoranthene, chrysene and benzo(g,h,i)perylene.

✓ In the unsaturated zone between 6 and 26 m (chalk), the PAH spectrum shows one more peak : the benzo(a)pyrene and a decrease of the intensity of the phenanthrene and fluoranthene peaks. The peak of benzo(a)pyrene is intensified in the saturated zone reaching around 25 % of the total PAH's at 50 m depth. This increase of the amount of benzo(a)pyrene at depth can be related to its physical properties. Indeed, amoung the 16 PAH's of the EPA list, benzo(a)pyrene has the highest liquid density with respect to water (1.282) and the lowest solubility in water (0.0045 $mg.L^{-1}$ at 25 °C).

The analyses of the 32 auger drillings reaching the chalk material (6 m depth) in the area of the pool tar have revealed three soil facies: brown, black and green, all highly contaminated with PAH (around 5000 $mg.kg^{-1}$ of dry soil for the 16 PAH sum). During a preliminary remediation phase, the bottom soil of the old tar pool has been deposited

on the site soil, directly around the basin. Two years after, the analysis of this material has revealed a high level of pollution by PAH's (more than 7000 $mg.kg^{-1}$ of dry soil). The PAH spectra of the three soil facies in place, and of the deposited excavated material are shown in figure 1.

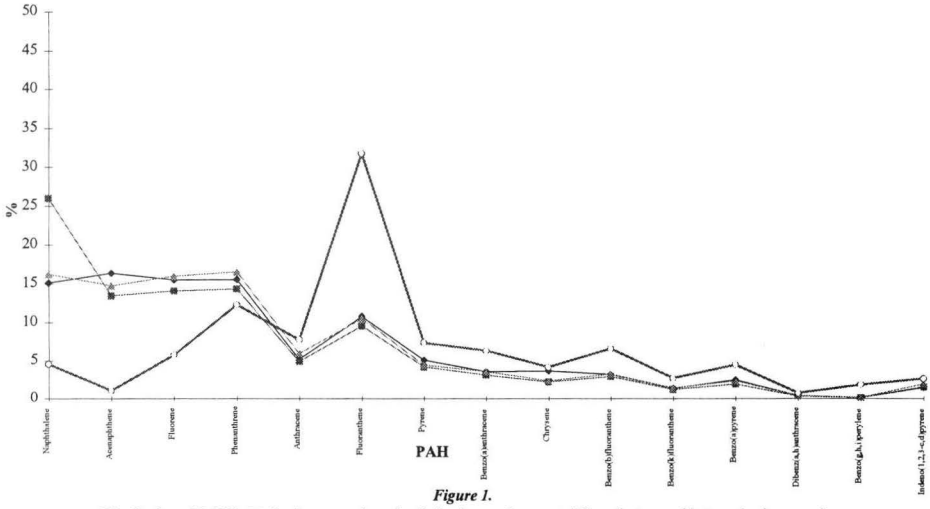


Figure 1.
Distribution of PAH in % for the contaminated soils in place and excavated from the tar pool bottom (vadose zone)
brown facies (200-220 cm) black facies (250-350 cm) green facies (350-450 cm) excavated soil

The three facies have the same PAH spectra with a plateau of high percentages for the four first compounds (the lightest) and a relative small peak of fluoranthene. It can be noticed the naphthalene peak in the black facies only (more than 25 %). This facies is located and confined under the old tar pool. The PAH spectrum of the excavated soil coming from the old tar pool bottom indicates a decrease of the amount of PAH's in naphthalene, acenaphthene and fluorene. This result can be explained by the relative volatility and solubility of these PAH's and their potential for natural attenuation, in this case accelerated by this « land-farming » disposal technique. Nevertheless, non considering the first part of the curve (light compounds), the spectrum shape is similar in the excavated material and in the three soil facies, showing probably the same origin of the PAH pollution.

The use of the spectrum variations for the description of a PAH polluted soil can be an interesting tool for the identification of the pollution sources. The analysis of the spectrum distorsion can give information on the assessment of the differential mobility of these contaminants in the subsurface. This method could be extended to the comparison of several sites polluted by PAH's.

SAMPLING AND HETEROGENEITY OF POLLUTED SOILS: THE ERROR ASSESSMENT

Ph. Wavrer[1], P. Lecomte[1], H. Védrine[2]

[1] CNRSSP - 930, Boulevard Lahure, BP 537, 59505 Douai cedex, France
[2] BRGM - Avenue Claude Guillemin, BP 6009, 45060 Orléans cedex, France

Keywords: Sampling methods, sampling techniques, heterogeneity, homogeneization, characterisation.

For the investigation of any possible polluted site, the soil sampling step is always decisive. Indeed, numerous decisions, with regards to risk assessment, safety conditions, remediation feasibility, environmental duties,... directly derive from analyses data of samples, so representing the most of actual available information. Moreover, experts have generally to provide their audit conclusion for the whole site, from only few sampling or observation points. As far as sampling is concerned the samples are to be **representative** facing the entire investigated site, ensuring the next analyses data.

To ensure a right sampling, the choice of the appropriate tool particularly in relation to its shape and size is actually an essential point. It is recommended to use a tool having at least three time the size of the biggest component likely to be found in the investigated medium, to avoid the pasting of fine particles along the drill walls or the segregation of coarse ones. As a next step, a sampling method minimizing the distribution heterogeneity has to be adviced in any case.

In spite of the carefull preparation step of technical choices for a sampling campaign, some sampling errors remain unavoidable. They all derive from the different heterogeneities of the sampling material and can be subdivided into three categories:

- The fundamental error, related to constitution heterogeneity. This directly depends on physical or chemical properties of the material. Blending or segregation have no effect on it. In fact, the fundamental error is an incompressible minimum under which it is impossible to give a variation range for a measurement carried out in a sample. To know this limit, it is then important to assess sampling performances; nevertheless, fundamental error is not to be assimilated to the total sampling error.

- The segregation error, related to the distribution of components - like a pollutant impregnating the soil matrix - in space or in time. Theorically, physical blending of the material tends to decrease this error, but such a homogeneization can be difficult to achieve in case of soils. Accordingly the suitable sample is sometimes more convenient to prepare by mixing a lot of unitary aliquots taken randomly.

- The taking and preparation errors, directly related to the sampling techniques and/or procedures such as taking, packaging, carriage...

Contaminated Soil '98, Thomas Telford, London, 1998, 827–828

Each of these three error components is illustrated with examples showing that representativity is difficult to assess and that it is essential to know, besides the State of the Art for techniques and tools, processes of soil formation and of pollutant distribution in it. The first study concerns a deserted steel industry site where the soil profile results from backfilling and the second one concerns an oil company site with a geological soil polluted by hydrocarbons.

In the first case, results showed that the quite high constitution heterogeneity makes it necessary to sample large masses of material in order to obtain enough precision with regards to soil composition. So widespread sizes and weights for blocks or fragments are observed (from few mm to m, and from few g to several tens of kg). Hence this leads to sample (and analyse) a minimum of four tons of material in order to reduce the fundamental error to minus 10%, and one ton to reduce it to 20%, assuming that other types of error are minimized in other respects.

The "natural" oil polluted soil, mainly made up of gravel and silt, is quite more homogenous as the largest grain size remains under 30 mm. In this way, a 5 kg taking warrants a 5% fundamental error for the grain size distribution.

The error of segregation has been studied considering the "natural" homogenous soil polluted by oil products, petrol and fuel. The migration of an organic pollutant percolating down into the soil clearly depends on its physical an chemical properties, but also on physical, chemical and biological properties of the soil itself, even in the case of a homogenous matrix.

In the studied example, petrol and fuel are distributed in a very heterogeneous way, in silt and gravel layers of the soil. So, major content variations are observed for both pollutants at the metric scale. In pits dug by mechanical showel, 4 series of 10 aliquots were taken along the walls, according to the soil profile and the type of pollutant. The results showed a very large range of variation, with a magnitude of 100 inside the same series. Randomly combining data by 2, 3, 4,... in each series, it was pointed out that at least 2 aliquots are needed to have a data variation lower than 100%, and 3 to 7 (according to the cases) to go down below 50%.

Finally, the influence of the tool has been studied for both situations. So usual tools for sampling polluted soils were tested, such as core drillings, augers, open pits,... Their respective performances were compared according to sampling depth, watertable level, volatility of pollutants, risk of cross contamination,... and their advantages and limitations recognized. The results evidenced that small size devices, such as manual augers or spoons are misfit in case of coarse grain sizes; it is particularly obvious for industrial sites, with filling material where blocks frequently occur. In this case, the use of a mechanical showel and the implementation of large-scale holes or trenches can significantly improve the equiprobability of samples.

As a conclusion, it can be said that even if the results obtained from these two cases are interesting and really usefull for field work, their generalization should be very carefully considered.

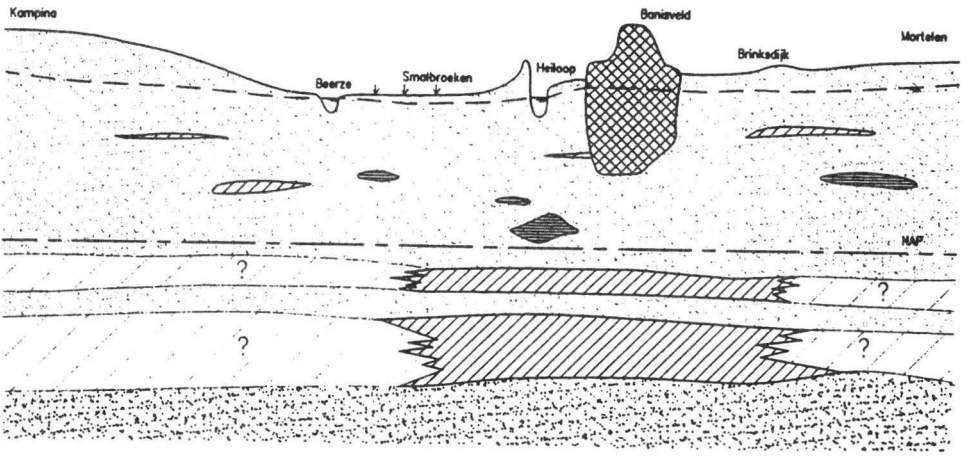
THE BANISVELD LANDFILL: A RESEARCH ON NATURAL ATTENUATION AND ECOLOGICAL EFFECTS

Slenders H.[1], Van Vossen W.[1], Kamsma T.[2]
[1]IWACO, Consultancy for water and environment, P.O.Box 525, 5201 AM, 's-Hertogenbosch (NL)
[2]Province North-Brabant, Department Soil, P.O. Box 90151, 5200 MC, 's-Hertogenbosch (NL)

Key words: abandoned waste disposal site, natural attenuation, plume, policies, groundwater modelling, ecological effects,

1. INTRODUCTION

The landfill "Banisveld" in the small town of Boxtel in the Province of North-Brabant in the Netherlands is situated in a zone between two nature reserves "De Mortelen" and "Kampina" (see figure). The little river Heiloop, which drains the area, intersects the zone. As a negative result the vulnerable bluegrass fields in the reserve "Kampina" are threatened with groundwater depletion. As a positive side effect of the draining function of the river, it partially catches the ground water contamination coming from the landfill. In the future, this zone is planned to become an ecological connection zone. At this moment the Netherlands Society for Nature and Environment is aiming at a filling up of the river, in order to stop the depletion of groundwater. As a result however, it is assumed that the ground water contamination can migrate to the bluegrass areas.



2. OBJECTIVES

The aim is to determine the biological and chemical processes in the subsoil at the former landfill. These processes contribute to the natural attenuation capacity of the subsoil. At two specific places these processes are regarded:

1. The transition zone between waste material and subsoil;
2. The different redox-zones within the contaminant plume in groundwater.

3. RESEARCH ACTIVITIES

For a part the study is based on the results of the Dutch NOBIS-project "in situ biodegradation at landfill sites" [lit.1]. For project Banisveld the following activities were carried out:

1. Soil sampling of the transition zone between waste material and soil. These samples have been analysed for the degrading capacity and the diversity of microbial species. No strict transition zone was found.

2. Gathering of hydro-geological data, groundwater flow, -direction and soil profile. A set of monitoring wells has been installed, sampled and analysed for an extensive set of parameters, giving information about redox-conditions, electron acceptors, donors, contaminants and the occurrence of intermediate products, results of bio-degradation.

4. RESULTS SO FAR

Although huge amounts of municipal waste were dumped, only low concentrations of contaminants were found. Change in redox-couples, conductivity etc. clearly indicates a leachate plume. Main processes are described.
In the transition zone between waste material and subsoil a diversity of degrading capacity was found, which at another site in the Netherlands seemed to have an optimal temperature of 10 degrees Celsius. The groundwater system was studied and a complex groundwater model was build. The river Heiloop shows a different influence in different seasons, it drains in winter and infiltrates in summer.
At this moment a conceptual model of the interaction between groundwater flow and processes is being build. The outcome of the study will result in general knowledge about the self-cleaning capacity of landfills and their surroundings. It will give insight in the possible effects of landfills as well as in the cost of aftercare and will play an important role in future policies on spatial planning and territorial approach in cases where landfills are involved. For the case Banisveld it will envisage the effects of the intended filling up of the river Heiloop.

6. REFERENCES

1. The intrinsic capacity of aquifers to degrade pollution from (old) landfills. IWACO-report 1073200, July 1997

STUDY OF TRANSFER MECHANISMS OF THE RESIDUES IN THE SOILS OF FORMER MANUFACTURED GAS PLANT SITES.

Philippe DELORME, Maryse CARLIER

Gaz De France - Research and Development Division - CERSTA - Environment Group
361 avenue du Président Wilson, BP 33, F-93211 La plaine Saint-Denis Cedex

Keywords : behaviour of contaminants, contaminated soil, PAH, soil permeability, groundwater flow

1. Introduction

Before the used of natural gas, since the beginning of the 60's, gas was produced by distillation from coal. The typical by-products were tar, phenols, ammoniac and iron cyanide. These by-products were valorized for example as raw materials of chemical industry. During the demolishing of the plants, the last by-products may remain and can be found cooped up in storage installation or mixed with soil. Gaz de France (the french national gas company), which is the owner of 467 former manufactured gas plant (MGP), has taken the full responsability to clean up these sites and to prevent any environmental consequence due to the possible presence of residues in the subsoil. A volontary agreement has been signed with the French Ministry of Environment, in order to program the investigations and to set an order of priority for studies on the sites. Following these investigations, a risk assessment, wich takes into account the future use of the site, is achieved for each site. The definition of the remediation and monitoring of the site is based on risk assessment.

2. Characterization of the pollution in the mineral phase

Observations and tests made on several soils of MGP sites (grain size analysis, binocular glass observations, X-rays diffraction, calcination at 300 or 500 °C and HPLC analysis) showed :
- the presence of pollutants in the soil creates coal tar soil aggregates,
- the results of calcination tests help to determine parameters of the grain soil coal tar aggregation state and so, can show the PAH absorption in some specific fractions of soil,
- in most of cases, the sandy grain size fraction (0.16 - 2.5 mm), majority in the sample, is less polluted than the fine fraction (silt and clay).

3. Mobility of the soil pollutants under groundwater flow

In order to study the mobility of soil pollutants in laboratory, several tests can be used. Water is the main contamination transfer vector of the chemical compounds with differents mechanisms (dissolving, leaching and diffusion). So, the laboratory tests used were flow or exchange simulations :
- leaching tests in order to determine the maximum leaching out,
- column and cell percolation tests, permeability of granular soils (ASTM D2434) in order to have a more realistic approach.

The results of the tests show :
❶ The presence of coal tar decrease strongly the natural soil permeability. This phenomenon is due to the trapping of PAH in the contaminated soil (Figure 1).
❷ The permeability of polluted soil, during column or cell percolation, decrease (Figure 1).

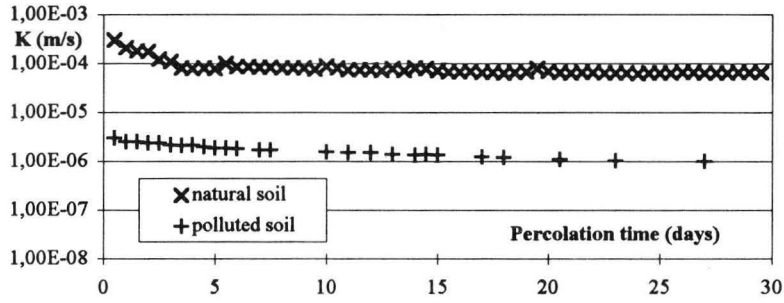


Figure 1

❸ Initial water content and compacting influence strongly the soil permeability. In particular, soil compacting limits the PAH mobility under a groundwater flow by closing soil pores. Conversely, ground digging works can bring an increase of the PAH mobility by decompacting the soil.

❹ Differences in PAH availability and accessibility can be noticed : In all percolation tests performed, we saw a strong decrease of PAH concentration in the percolated water (Figure 2). The trapping of PAH in aggregates can explain this phenomenon.

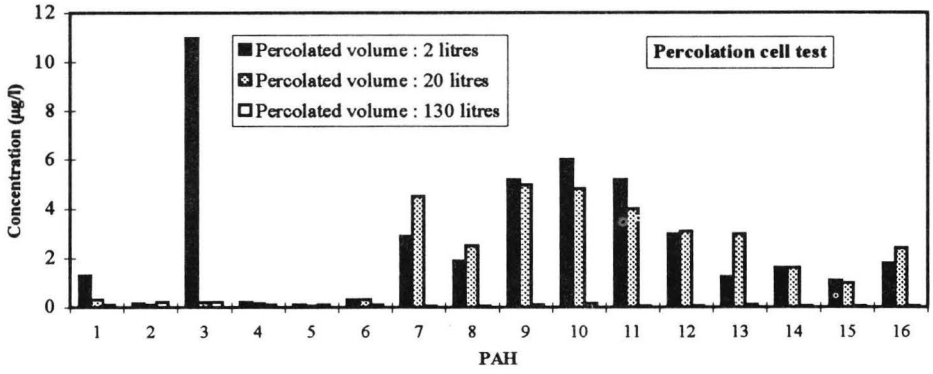


Figure 2

❺ The main way to mobilize PAH in polluted soils is the solubility state. But, another significant way is also an ultra-fine phase transfer (lower than 40 µm, like clay for example) where PAH are fixed by adsorption.

4. Conclusion

The results of these studies bring useful informations on the transfer mechanisms of pollutants, in particular :

- soil compacting and soil permeability are the key points of the transfer mechanisms of contaminated soil by PAH,
- many components in the residues show little mobility and are naturally stabilised in the soil,
- a "mobilization accessibility" phenomenon of some PAH seems to exist.

These results, in accordance to "in-situ" observations and measurements, can provide useful information to explain the contaminants current localization and to predict, with more and less accuracy, the behaviour of these contaminants.

EXAMINATION OF MINERAL OIL CONTAMINATED SOILS BY MEANS OF THIN-LAYER CHROMATOGRAPHY

Ch. Reimers

Department of Waste Management, Technical University of Hamburg-Harburg, Harburger Schloßstr. 37, 21079 Hamburg, Germany

Key words: contaminated soils, thin-layer chromatography, PAH, mineral oil hydrocarbons

Recording the extent of a contamination and the kind of pollutants as well as assessing the efficiency of a remedial process require extensive chemical analyses. In addition to quantifying the universal oil hydrocarbon content it is important in mineral oil analytics to determine the polycyclic aromatic hydrocarbons (PAH). While the content of mineral oil hydrocarbon is determined in general as a sum parameter following the DEV H 18 by means of IR spectroscopy applying chlorofluoro carbon, extensive analyses by means of GC or HPLC are necessary for the determination of individual compounds like PAH's. Furthermore, the application of freon as solvent has to be considered as critical - according to the H 18 method - for reasons of environmental compatibility. A universal method which gains more and more importance in environmental analytics because of the rapidly progressing automation and because of the various application possibilities, is the thin-layer chromatography.

The thin-layer chromatography is very flexible regarding the choice of solvents and thus independent of the use of halogenated compounds. This method is characterised by a low consumption of solvents and fast analyses of many samples on one plate are the remarkable features.

Mineral Oil Hydrocarbons

The determination of mineral oil hydrocarbons (aliphatic compounds and naphthenes) of medium and low volatility in soil samples is based on their separation and quantitative evaluation. It can be made visually or densitometrically by means of a thin-layer scanner. The advantage of the method lies in its low requirements pertaining to apparatus and chemicals as well as in its rapidness which makes it suitable for quick in-situ analyses as for example for the assessment of the mineral oil content of a contaminated site.

The principle of the determination is the separation of the aliphatic hydrocarbons from other substance groups. After the staining the mineral oil hydrocarbons appear as spots approx. 0.5 to 1.0 cm below the solvent front (Rf value approx. 0.8). Comparing the results of the thin-layer chromatographic determination of the mineral oil hydrocarbon content of real

contaminations presented hereafter with those of IR spectroscopic determination according to DEV H18 shows good agreement of the methods (Table 1).

Table 1: Thin-layer chromatographic determination of the mineral oil hydrocarbon content of real contaminations compared with the IR spectroscopic determination according to DEV H18

Sample	TLC [g/kg]	DEV H 18 [g/kg]
1	22.6	20.9
2	15.6	18.9
3	0.08	n.d.
4	33.0	28.8
5	0.11	0.11
6	1.20	1.30
7	0.40	0.52
8	0.30	0.24

Polycyclic aromatic hydrocarbons (PAH)

The thin-layer chromatography turns out to be very sensitive in combination with the fluorescence detection. Apart from quickly providing results concerning the existence of a contamination, the thin-layer chromatography facilitates conclusions about the distribution and the extent of the contamination for first screening investigations. This method also gives information about specific and extensive analyses by means of GC or HPLC.

During the investigations, various static phases and mobile phase systems in different combinations were used. As most suitable proved to be three systems enabling a separation of the 16 EPA-PAH into five or six PAH groups. A specific postchromatographic treatment of the thin-layer plate also causes an intensification of the fluorescence. In addition an impregnation of the PAH can be achieved. In case there are multicomponent mixtures and a strong loading of the thin-layer, an overlap of substances cannot be completely excluded .

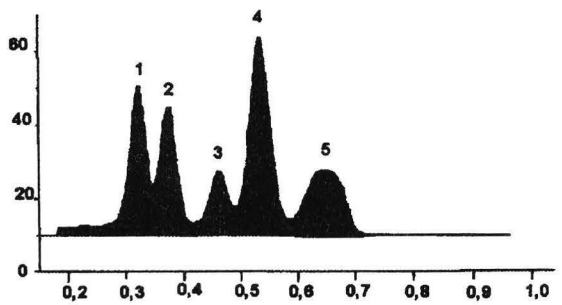


figure 1: separation of PAH into five groups; RP 18-phase, hexane/dichloromethane 95/5, fluorescence detection 366 / 400 nm

1: dibenzo(a,h)anthracene, benzo(g,h,i)perylen, indeno(1,2,3-c,d)pyrene
2: benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene
3: chrysene, benzo(a)anthracene
4: fluoranthene, pyrene
5: phenanthrene, anthracene, fluorene

COMPARISON OF *EX SITU* AND *IN SITU* BIODEGRADATION MEASUREMENTS FOR MONITORING BIOREMEDIATION

I. Haider[1], E. Al-Saleh[1], C. Henkler[1], C. Fenwick[1], E. Bär[2], R. Henkler[3] and J.R. Mason[1]

[1] Division of Life Sciences, King's College London, Campden Hill Road, London W8 7AH, UK.
[2] Sachverständigenbro Eckart Bär, Scharrenbroicher Sraße 44, 51503 Rösrath, Germany
[3] ICI Paints, Wexham Road, Slough SL2 5DS, UK

Key words: aromatic hydrocarbons, biodegradation, BTEX, characterization, contaminated site, *in situ* bioremediation, microorganisms, soil and groundwater contamination

SUMMARY

Sediment samples taken from a BTEX-contaminated site were characterized by the traditional methods of estimating the number of toluene degrading bacteria and *ex situ* ^{14}C-toluene mineralization and, by the extraction and PCR amplification of DNA encoding the genes for degradative enzymes (Class IIB dioxygenases). The latter two methods show good agreement.

BACKGROUND

Aromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylene (BTEX) have been used in many industrial processes, including paint manufacture. Frequently BTEX have been detected in the soil of manufacturing sites, requiring remediation to prevent contamination of the groundwater. One such remediation strategy uses the indigenous microorganisms to oxidize these hydrocarbons *in situ*. Successful implementation of any bioremediation process requires a detailed characterization of the *in situ* biodegradation activity, to demonstrate the efficacy of the treatment and assess whether bioaugmentation or nutrient addition is worthwhile. To date, many assessments of bioactivity report *ex situ* measurements of microbial metabolism. Recent developments allow monitoring of *in situ* levels of specific catabolic genes and their expression, by direct isolation of DNA and mRNA from contaminated soils (Fleming *et al.*, 1993). Quantification of DNA by polymerase chain reaction (PCR) and and of mRNA by reverse transcriptase-PCR, enables the estimation of biodegradative potential (presence of gene) and biodegradative activity (expression of gene), respectively.

MATERIALS ANDS METHODS

Boreholes were drilled across a BTEX-contaminated site and sediment samples taken at intervals of 1m to a depth of 15m. Samples were maintained at 4°C (for estimation of numbers of toluene degrading microorganisms and the rate of ^{14}C-toluene mineralization) or flash frozen in liquid nitrogen and stored at -75°C (for nucleic acid extraction).

RESULTS AND DISCUSSION

Seven pairs of PCR primers, specific for genes encoding aromatic hydrocarbon-degrading enzymes, were designed and screened against microorganisms isolated from the BTEX-contaminated site. Those specific for the α-subunit of Class IIB dioxygenases (Mason and Cammack, 1992) had the broadest specificity, amplifying a 521bp band from over 60% of the strains examined.

Comparison of Ex Situ (Substrate Mineralization) and In Situ (PCR) Estimation of Biodegradative Potential.

Ex situ mineralization was measured as the rate of $^{14}CO_2$ evolution from ^{14}Cmethyl-labelled toluene. *In situ* biodegradative potential was estimated by PCR amplification of DNA isolated directly from sediment samples. Comparison of these results (Figure 1) shows a clear relationship between the two protocols with regions of high biodegradative potential at depths 4-6m, 8-10m and 12-15m. In contrast bacterial counts obtained from sediment samples incubated on Hutner's minimal medium with toluene as the sole carbon and energy source did not show the same trends.

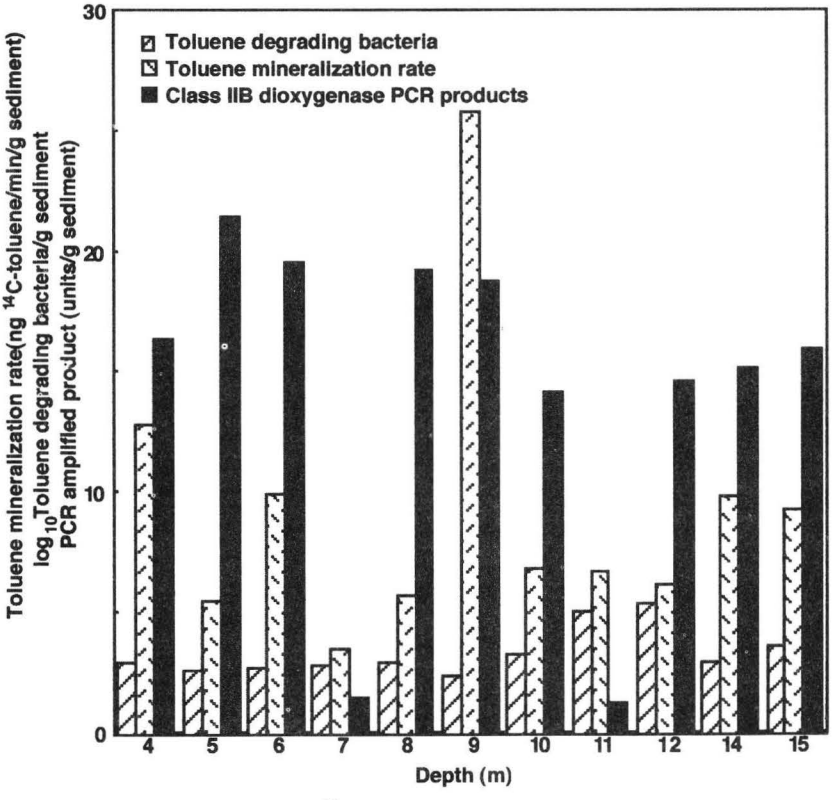


Figure 1. Comparison of *ex situ* (^{14}C methyl-labelled toluene mineralization and viable counts) and *in situ* (PCR amplification of genes encoding Class IIB dioxygenases) estimation of biodegradative potential in sediment samples taken from a BTEX-contaminated site.

RERERENCES

Fleming, J.T., Sanseverino, J. and Sayler, G.S. (1993) Quantitative relationship between naphthalene catabolic gene frequency and expression in predicting PAH degradation in soils at town gas manufacturing sites. Env. Sci. Technol. 27:1068-1074

Mason, J.R. & Cammack, R. (1992) The electron-transport proteins of hydroxylating bacterial dioxygenases. Annu. Rev. Microbiol. 46, 277-305

ACKNOWLEDGEMENTS

This work was supported in part by a grant from ICI Paints Ltd and a research studentship from the government of Kuwait to EA.

METAL POLLUTION DETECTED BY INFRARED SPECTROSCOPY OF CONTAMINATED SOILS

N. Dupuy[1], A. Semmoud[1], D. Maniez[1], T. Sterckeman[2], J.P. Huvenne[1]
1 LASIR-CNRS UPR 2631L Bat C5 USTL, 59655 Villeneuve d'Ascq, France
2 Laboratoire d'analyse des sols INRA, 273 rue de Cambrai , 62000 Arras, France

Key words: Contaminated soil, metal, in-situ measurement technique, organic matter, physico-chemical processing

SUMMARY
The paper presents a classification of soil sampless with respect to the level of metal pollution determined by chemometrics treatment of ATR-FTIR spectra.

INTRODUCTION

The determination of metal content in polluted soils by using conventional laboratory techniques such as ICP or atomic absorption spectrophotometry is tedious and requires sample handing. For several years, the use of infrared spectroscopy has been well known as a powerful analytical tool[1]. Since the metal cations do not absorb mid infrared light, we wanted to characterise them using their interaction with organic matter in soils[2,3] Combined with the use of new sampling techniques such as ATR (Attenuated Total Reflection) cells, MIR spectroscopy has been considerably applied[4] for the classification of mid-IR spectra by principal component analysis (PCA) [5,6,7]. The aim of work was to evaluate the use of PCA analysis for the classification of contaminated soils.

RESULTS

The study concerns 38 samples of soil from the region " Nord Pas de Calais " in France. They dot not contain more than g/kg of $CaCO_3$ they have been analysed by atomic methods and the total concentration in metal allows to gather samples in tree groups : sample noted a contained more than 600mg/kg, sample noted b between 600 and 400mg/kg and sample noted c less than 400mg/kg.

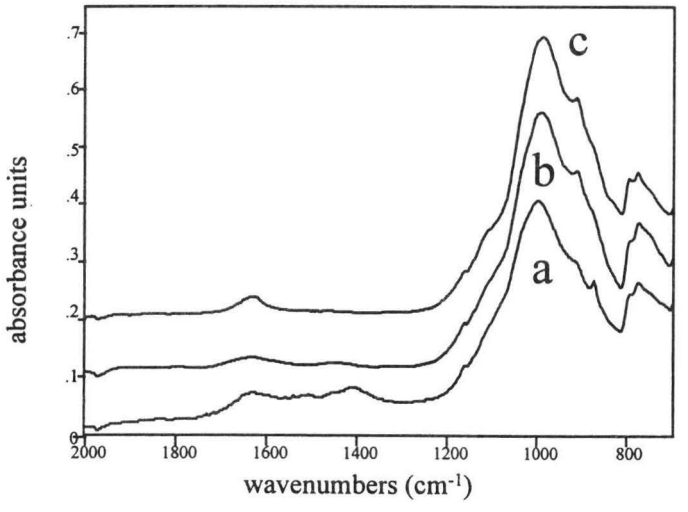


Figure 1 :

ATR-FTIR spectra of soil samples.

The ATR spectra are obtained with a horizontal diamond crystal accessory, named "golden gate" equipped with a press to bring pressure to bear on the sample. A reference spectrum of the crystal is collected before collection of each sample spectrum. Since only 200mg of matter is used to record the spectra, reproducibility is not excellent. So we propose to use for data treatment the average of five measured spectra in order to decrease the effect of heterogeneity. In these conditions coefficient of variation of the band intensity of 10 spectra of the same soil is about 5%. When we compare three spectra which represent the three groups previously defined, we can see that they are very similar to each other.
The principal constituents of soils are silicates with very intense bands in the 1200-900 cm^{-1} region. As the profile of humic acids are dominated by two very prominent bands [8] appearing at around 1600 and 1400 cm^{-1}, the principal component analysis is performed in the 2000-1250 cm^{-1}region. The scattergram obtained with the second and third components is shown in figure 2. All the samples are correctly classified into three groups according to their degree of pollution.

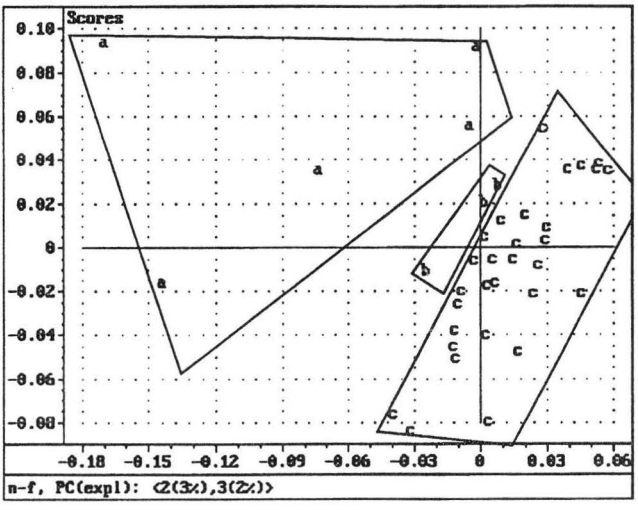


Figure 2 :

Scattergram on the second and the third principal components

CONCLUSION

A convenient method for identifying polluted soils without any chemical separation and any a priori knowledge about their composition is presented. On the basis of their IR spectra, soils are separated into three classes according to their degree of pollution.

The authors thank the council of the region "Nord Pas de Calais" to support this work within the concerted research program "Sites et sols pollués"

RERENCES

1. Dupuy, N., Duponchel, L. , Huvenne, J.P. and Legrand, P. (1994) J. Chemom.8,333
2. Stevenson, F.J.,(1982) Humus Chemistry, Wiley, N.Y.
3. Gamble, D.S., Schinizer, H. and Skinner, D.S. (1977) Can. J. Chem.54, 47
4. Cadet,F., Robert, C. and Offman, B. (1997) Appl. Spectrosc. 51, 369
5. Dupuy, N., Duponchel, L. , Huvenne, J.P. et Legrand,P. (1996) Food Chemistry57,245
6. Naes, T. and Hildrum, K.I. (1997) Appl. Spectrosc. 51,3
7. Hasenoehrl,E.J. and Griffiths,P.R. (1993) Appl. Spectrosc. 47,5
8. Francioso, O.,Ciavatta, C., Sitti, L. and Gessa, C; (1996) Appl. Spectrosc. 50,9

CONTRIBUTION OF *LUX*-BACTERIAL BIOSENSORS TO REMEDIATION OF BTEX CONTAMINATED LAND

S. Sousa[1], H. Weitz[2], C. Duffy[1] , E. Bär[4], R. Henkler[3], B.N. Anderson[5], J.R. Mason[6], L.A. Glover[2] and K. Killham[1]

[1]*Department of Plant and Soil Science, University of Aberdeen, Cruickshank Building, St. Machar Drive, Aberdeen, AB24 3UU.* [2]*Department of Molecular and Cell Biology, Institute of Medical Sciences, Forester Hill, University of Aberdeen, Aberdeen AB25 2ZD.* [3]*ICI Paints, Wexham Road, Slough SL2 5DS, UK.* [4]*Environmental Expert Office, Rösrath, Germany.*[5]*Department of Chemical and Metallurgical Engineering, RMIT University, Melbourne, Australia.* [6]*Life Sciences Division, King's College London, W8 7AH, UK.*

Key words: BTEX, soil and groundwater contamination, *in-situ* bioremediation, monitoring, genetically engineered microorganisms (GEMs), biosensors

SUMMARY

Luminescence-based bacterial biosensors (*lux*-marked *Escherichia coli* and *lux Pseudomonas putida* F1) were used to identify constraints to bioremediation of BTEX contaminated land. The approach, involving sequential exposure of sensors to samples treated by a series of manipulations, was validated by correlating biosensor response with mineralisation of ^{14}C-labelled toluene.

INTRODUCTION

Bioremediation of contaminated land is often restricted by chemical and physical constraints (Bouwer *et al.*, 1994). Rapid and reliable techniques are required for assessment of the remediation potential and identification of the nature of the constraints. In this study, the scope for *lux*-marked bacterial biosensors to provide this assessment was evaluated. A range of bacteria, including an isolate from a BTEX contaminated site, were marked with the *luxCDABE* genes using the multi-copy plasmid pUCD607. A BTEX toxicity assay was developed where freeze-dried *lux* bacterial biosensors were resuscitated prior to sample exposure and subsequent light output was measured using an automated luminometer. Light output response from the biosensors provided sensitive detection of BTEX in the parts per billion range in some cases (Boyd *et al.*, 1997).

MATERIALS AND METHODS

Boreholes were drilled across a BTEX contaminated site, with sediment and groundwater samples obtained at different depths down to 15 m. Precautions were taken to avoid BTEX losses. A series of sample manipulations linked to biosensor responses was developed to identify potential constraints to site remediation. Manipulations included N_2 sparging, pH adjustment, filtration, oxygenation and muffle furnacing. Biosensor response to untreated samples reflected the total toxicity. Sparging with nitrogen allowed for rapid removal of volatile organics present and the muffle furnace treatment removed any non-volatile organics remaining, providing a final residue containing inorganic pollutants, such as heavy metals.

Contaminated Soil '98, Thomas Telford, London, 1998, 839–840

RESULTS AND DISCUSSION

Toxicity results are shown as % maximum bioluminescence, being the maximum calculated against a blank of double deionised water at pH 5.5. Toxicity causes a reduction in light production due its effects on metabolic activity of the cells, and this reduction is proportional to the concentration of the pollutant present. The *lux* biosensors identified some underlying toxicity in some sediment and water samples (table 1) of inorganic, non-volatile and volatile organic nature, as well as a pH constraint.

Table 1. Percentage maximum bioluminescence of groundwater (W1 and W2) and sediment samples (S1 and S2) from a BTEX contaminated site, untreated and after nitrogen sparging, pH adjustment, muffle furnacing and filtration (the % in brackets are coefficients of variance)

sample	no sparge	N_2 sparge	pH adjustment	muffle furnace	filtration 0.22 µm	filtration/ N_2 sparge
W1	5.78 (5%)	42.01 (8%)	21.75 (5%)	87.80 (3%)	77.14 (9%)	81.03 (7%)
W2	89.72 (1%)	95.19 (3%)	85.24 (2%)	95.29 (3%)	87.58 (6%)	85.41 (6%)
S1	50.34 (5%)	74.69 (11%)	79.55 (3%)	96.26 (3%)	-	-
S2	3.23 (25%)	10.20 (9%)	68.33 (4%)	72.40 (2%)	-	-

Sample W1 showed high toxicity and results obtained by different treatments were significantly different with the exception of the two filtration steps (P-value> 0.05). Toxicity was significantly reduced after elimination of VOC's by nitrogen sparging. Bioluminescence was further increased after muffle furnacing removed all organic matter present and removed toxicity due to non-volatile organic pollutants. This suggested there is a possible constraint to remediation due to non-VOC's. Toxicity was decreased by filtration, demonstrating some toxicity was related to suspended solids present in the water sample. The light response of the *lux* biosensors on exposure to these samples correlated strongly with standard chemical analysis, demonstrating the value of the biosensors for rapid diagnosis of BTEX plumes. Furthermore, strong correlation of sensor response with rate of mineralisation of ^{14}C-toluene (data not shown) provided some validation of the use of this approach to identify constraints to bioremediation.

CONCLUSIONS

The use of the *lux* biosensor in conjunction with sample manipulation allowed classification of sample toxicity into broad categories. Identification (and possible alleviation) of constraints represents a potentially major contribution of *lux* bacterial biosensors to the management of BTEX contaminated sites undergoing remediation

ACKNOWLEDGEMENTS

The Portuguese Government (Praxis XXI, Sub-programa Ciência e Tecnologia do 2° Quadro Comunitário de Apoio) is acknowledged for provision of funding for S.S. ICI Slough UK is acknowledged for provision of funding for H.W. and C.D.

REFERENCES

Bouwer, E., Durant, N., Wilson, L., Zhang, W. and Cunningham, A. 1994. Degradation of xenobiotic compounds *in situ*: capabilities and limits. *FEMS Microbiol Rev.* 15: 307-317.

Boyd, E.M., Meharg, A.A. and Killham, K. 1997. Toxicological assessment of benzene and its primary degradation biproducts using a *lux* modified bacterial biosensor. *Environ Toxicol Chem.* 16: 849-856.

Problems Arising From The Lack Of Standardised Methods For Soil Analysis.

James A. Pickard, City Analytical Services plc, 3 Fairfield Court, Wheler Road, Coventry, U.K., CV3 4LA

Keywords: Analytical methods, heavy metals, phenols, standardisation.

One of the biggest problems associated with the analysis of contaminated land and the subsequent evaluation of analytical results is the lack of standardised analytical methods.

There are a large number of techniques available for the analysis of virtually any determinand which can yield widely varying results. This can obviously have an impact when it comes to assessing the degree of contamination of a site and specifying remedial works.

The problem is further exacerbated by the nomenclature used in reporting, e.g. "total" metals, "total" cyanide, etc. and a lack of understanding on the part of the individuals using the data.

To take two examples to illustrate the sorts of difficulties encountered in the analysis of a) groups of organic compounds and b) metals:-

1) Phenols.

The most commonly used techniques for the routine analysis of phenols in soil are colorimetry (usually after steam distillation) and either liquid or gas chromatography after extraction into a methanol/water mixture. The first yields a result only for those phenols which are steam distillable, i.e. primarily monohydric phenols. The colorimetric procedure using 4-aminoantipyrine gives varying molar absorptivities for different phenols and does not give a reaction with para-cresol, an important and common contaminant. The results are all expressed as a single compound, usually phenol itself. The chromatographic procedures yield "better" results and can be reported as individual compounds or groups of compounds, e.g. phenol, cresols, xylenols etc. Chlorinated phenols, of which pentachlorophenol (PCP) is a common contaminant associated with timber treatment, are not however detected by either of these methods.

2) Metals.

Results for metal analyses are almost always referred to or reported as "total" but there are many techniques for the extraction of metals from a soil matrix. These techniques range from the draft ISO method involving refluxing with aqua regia, through microwave assisted digestion to a simple open digestion on a hotplate. All of these methods may utilise a wide range of acid mixtures which can include aqua regia alone or mixed with hydrofluoric acid, perchloric acid, boric acid, hydrogen peroxide etc.
There are also methods using solid fusion with reagents such as sodium peroxodisulphate. Each of these extraction methods will give widely varying results for individual metal concentrations. The problem is compounded by the fact that the

Contaminated Soil '98, Thomas Telford, London, 1998, 841–842

extraction procedure used for the analysis of certified reference materials (CRMs) is often not known (or not stated) and hence the validity of analytical results is therefore difficult to establish.

The two examples cited above indicate the need for two courses of action; firstly, analytical methods must be standardised so that legislators and users of data can be assured that they are indeed comparing like with like. Secondly there needs to be a process of education so that data users are aware of the potential pitfalls when examining analytical results. This is especially important in an international context when scientists or engineers from one country may be using results obtained elsewhere for the design of remediation projects or referring to national limit values which may have been derived from analyses using completely different analytical methods.

The problem also extends into sample preparation techniques. Samples may be air- or oven-dried and subsequently ground to pass a variety of sieve sizes, depending upon the national standard used.

It is, therefore, vitally important that reports contain all of the information relating to sample preparation, extraction and analytical methods so that the end user of the data can be certain that a valid comparison can be made.

TRANSFER OF C_6H_6, C_2H_5OH, CCl_4 AND WATER IN NON-ISOTHERMAL SOIL

A.M.Globus[1]

[1] Agrophysical Research Inst., Grazhdansky pr.,14,
St.Petersburg 195220, Russia

Key words: non-isothermal transfer, unsaturated soil, benzene, ethanol, carbon tetrachloride

SUMMARY

Time rates of thermal transfer of water, C_2H_5OH, C_6H_6 , CCl_4 and dibutylphtalate $C_{16}H_{22}O_4$ were measured in unsaturated soils and porous granular ceramic materials. The time rates were higher than calculated thermal vapor diffusion rates (TVDR). The larger are TVDR the smaller are the differences and the broader is moisture content range of effective thermal mass transfer.

Exchange of soils with atmosphere usually takes place through unsaturated zone, where temperature gradient is a one of moving forces. Importance of thermal mass transfer lays in its ability to contribute significally in such a moisture content range where the transfer of liquid phase is negligible.

It is well known that the time rate of water thermal transfer in a definite range of moisture content range exceeds significally the velocity of classical thermal vapor diffusion. Widely adopted explanation of the phenomenon – Philip-de Vries hypothesis of series-parallel transfer – includes four constituents: 1) increased temperature gradient in water-free pores as compared with average gradient in the medium; 2) interaction of vapor and liquid fluxes inside the pores; 3) increased cross-section for the transfer due to this interaction; 4) thermocapillary transit liquid flow. We showed that experimental data for water in various porous media comply with first three constituents.

A very few is known however on thermal mass transfer of fugitive liquids other than water. The respective research can supply the actual data and elucidate a nature of transfer mechanisms . We studied thermal transfer of water, C_2H_5OH, C_6H_6 , CCl_4 and dibutylphtalate $C_{16}H_{22}O_4$ (the latter – as an example of liquid with very low vapor pressure) in closed horizontal columns of unsaturated loamy soils and porous granular ceramic materials as models of structured soils at mean temperature 27°C and temperature gradient 1.0°C/cm.

Thermal vapor diffusion – leading link of Philip-deVries mechanism - has to be proportional to the product ξ:

$$\xi = \mathbf{DP/(P-p)}\ \partial c/\partial T \qquad (1)$$

where D –coefficient of diffusion in air, P –ambient pressure, p –vapor pressure, c - concentration of saturated vapor, T – temperature.

Thermocapillary flux is to be proportional to the product ε:

$$\varepsilon = \rho/\eta\ )\ \partial\sigma/\partial T \qquad (2)$$

where ρ - density of a liquid, η - its viscosity, σ - its surface tension. Values of ξ and ε for the substances mentioned above are given in the Table 1.

Table 1

Values of products ξ and ε, responsible for thermal vapor diffusion and thermocapillary flows respectively.

Substance	ξ x10^{-7}, g /(cm s °C)	ε x10^{-2}, g/(cm^2 s °C)
H_2O	3.6	18.2
C_2H_5OH	10.8	6.8
C_6H_6	21.5	20.8
CCl_4	38.9	20.1
$C_{16}H_{22}O_4$	10^{-5}	39.5

Table 2

Measured time rates of thermal moisture transfer in granular ceramics and their ratios to time rate of thermal vapor diffusion

Substance	Measured rate, g/(cm^2 s)x10^{-7}	Ratio of measured rate to that of thermal vapor diffusion
H_2O	8.9	5.3
C_2H_5OH	12.0	2.4
C_6H_6	17.6	1.8
CCl_4	30.3	1.7
$C_{16}H_{22}O_4$	0	-

Evidently, the substances represent two different sequences thus enabling to determine the leading mechanism of thermal mass transfer from experimentally measured time rates. For all the media studied the latter were larger than thermal vapor diffusion velocities however formed the same sequence as -values (Table 2). Moisture content range, where thermal mass transfer can compete with a liquid flow, also broadens proportionally to ξ . In the same time the *ratios* of rates measured to the rates of pure thermal vapor diffusion are smaller the larger are their ξ-values. This can be explained at least partly by diminishing of latent heats of the substances in the same order. This parameter influences the link 1 in the picture of series-parallel mechanism.

THE POTENTIAL THREAT TO GROUNDWATER SUPPLIES FROM THE FUEL ADDITIVE MTBE

J Turrell and K Blackmore

WRc plc, Henley Road, Medmenham, Marlow, Buckinghamshire, SL7 2HD, UK

Key words: Petrol hydrocarbons, environmental impact, monitoring, groundwater

Summary
MTBE (methyl tertiary butyl ether), a very soluble and potentially major additive in petrol, has the potential to contaminate groundwater resources through spills and leaking underground pipes and storage tanks. Although consumption is increasing there is currently little widespread awareness of the threat posed by MTBE to groundwater quality, and its ultimate fate in the environment. The lack of structured monitoring within the UK means there is only very limited data on the occurrence of MTBE in groundwater, even though it has been used extensively for ten years. It is possible that there has not been time for groundwater systems to show MTBE contamination, it is also likely that many incidents have gone undetected. It is clear from the persistence, mobility, high solubility, and apparent lack of degradation of MTBE it should have a higher profile in monitoring groundwater than it does at present.

Introduction

The emission of lead from internal combustion engines, arising from the use of alkyl-lead compounds, used as anti-knock additives in petroleum, was considered cause for environmental concern, firstly in the US in the late 1970s and then subsequently in the UK. The subsequent phase-down of lead in petroleum in the last decade has had a major effect on the composition of petroleum in both the US and the UK. MTBE was originally introduced as an octane-blending component, to replace the 'lost' lead in petrol. Its primary use today has started to change to that of a clean air component, where MTBE is used for its oxygen content as refiners have to reformulate petroleum to meet new environmental legislation.

At the present time the lack of legislative restrictions in Europe leave the refiners free to use cheaper alternative high aromatic octane stocks. UK refiners are currently adding only 0.1% to 1.0% MTBE to standard unleaded and leaded petroleum grades. Its high cost dictates that it is only added in significant quantities to create the Super unleaded grades of petroleum, where the high octane number required can only be met using ether and alcohol additives. It is likely, however, that MTBE levels in petrol are set to rise to between 5-15% MTBE when proposed changes in Clean Air Legislation in Europe are implemented. Although MTBE is not a component of all UK petrol, it is currently added to about 40% of petrol blends.

Fate and Behaviour

Although there is no doubt that MTBE and ether additives have the potential to contaminate groundwater, the addition of MTBE in petrol blends effectively leads to a

reduction in the total aromatic and therefore carcinogenic content of petrol, in addition to reducing toxic emissions from vehicle exhausts. The move towards increased MTBE consumption in petrol on these grounds could therefore be a good one. In addition, ethers:

- are relatively non-toxic, although the low taste and odour thresholds (5-15 $\mu g\ l^{-1}$) of MTBE pose a problem if contaminated groundwater is used for drinking water.
- are readily detected by taste and odour.
- migrate faster than other hydrophobic constituents of a petroleum spill, and hence they are often the only detectable contaminant at the outer fringes of the total plume and could therefore provide an early warning of more toxic aromatic contaminants from a petroleum leak or spill.
- exhibit high water solubilities in a single component system which will be significantly reduced when part of a petroleum mixture. Observed solubility is also significantly reduced at the temperature of groundwater.
- reduce observed aqueous concentrations of more toxic BTEX components in a petroleum spill.

Although existing information indicates that spills from oxygenated fuels appear to be no more environmentally damaging than from non-oxygenated fuels:

- MTBE is more soluble than other components of petroleum and will consequently travel further, contaminating a larger area than an unblended petroleum spill;
- they often constitute the largest component of a petroleum spill;
- MTBE has a lower sorption onto soil and sediment particles due to its enhanced solubility, and also has a slow rate of hydrolysis. Therefore it will remain in the groundwater environment longer.

Future monitoring requirements

The project highlighted the sparsity of information that is available on the occurrence of MTBE in UK groundwaters; data for many Regions are non-existent. There is no routine monitoring undertaken in the UK for MTBE and consequently there are insufficient data on which to make any accurate assessment of the current risk posed by MTBE to UK groundwater resources. It is clear from the persistence, mobility, high solubility, and apparent lack of degradation of MTBE that it should have a higher profile in monitoring groundwater than it does at present. A structured baseline monitoring programme is required to provide data to understand the life cycle of MTBE in the water environment, and in order to enable sound aquifer protection policies to be developed. Specific questions related to the transport of MTBE which will determine if MTBE concentrations are likely to rise above current levels, and which need to be answered are:

1. the PATHWAYS by which MTBE enters the ground;
2. the PROCESSES by which it is transported in groundwater; and
3. the RATES at which it degrades.

FIRST RESULTS OF EXAFS-SPECTROSCOPY AND SEM/EDX INVESTIGATIONS ON HEAVY METAL CONTAMINATED SOILS AS A TOOL FOR DIRECT SPECIATION ANALYSIS

E. Welter, W. Calmano, S. Mangold

Dept. of Environmental Science and Technology, Technical University of Hamburg - Harburg, Eissendorfer Str. 40, D-21073 Hamburg, Germany

Key words: analytical methods, availability, contaminated soil, heavy metals, lead

Summary
XAFS and SEM/EDX were used to perform heavy metal species analysis in contaminated soils. It will be discussed how the XAFS inherent information about the chemical environment of an absorbing element can be extracted from the XANES and EXAFS-region of XAFS-spectra. SEM/EDX-analyses can serve as additional analytical method, if the samples meet certain requirements.

Introduction

Knowledge about the chemical binding form of heavy metals in contaminated soils is important for the assessment whether and how a contaminated site has to be cleaned. The most widespread used methods for speciation analysis in soils and sediments are sequential extraction procedures. Because the used extractants do not show a high selectivity for certain metal compounds, sequential extractions only yield up to 5 or 6 operationally defined groups of more or less soluble species [1]. In addition to that the first steps of a sequential extraction alter the composition of the samples, so that consecutive steps do not give information about the natural sample.
Possible analytical methods for the determination of actual heavy metal compounds in soils or sediments have to fulfil the following fundamental requirements:
- They have to yield at least information about the oxidation state of the heavy metal
- They have to be performable in the original matrix and under mild conditions, to minimise the risk of alteration of the sample composition

One method that meets these basic requirements to a very high degree is XAFS-spectroscopy [2].

Experimental

Pb L_3-X-Ray Absorption Fine Structure Spectra (XAFS) were recorded at the HASYLAB at DESY (Hamburg Germany) on beamline X1.1, experimental station Römo 2. The XAFS-spectra were recorded between 12800 and 13800 eV, thus covering the XANES and EXAFS-region of the Pb L_3-X-ray absorption spectrum. The samples were prepared by mixing thoroughly grinded soil samples with boronnitride as bonding agent and pressing pellets of 1 cm diameter and 1 mm thickness in a KBr-press. The samples originated from the vicinity of a battery factory in Hannover, Germany. Reference samples were prepared by mixing the respective reference compounds with BN and forming pellets. All spectra were recorded at room temperature.
Linear combinations of reference substance spectra were used to identify the lead compounds in the soil samples. The best fit was calculated by the least mean square error method

SEM/EDX measurements were performed on a JEOL 840 SEM equipped with a LINK LZ5 EDX-detector. Samples were either coated with a 15 nm goldlayer, or if EDX analyses should be performed, used without coating.

Results and discussion

Fig. 1 shows the XANES-spectra of 5 $PbCO_3$ and PbO containing mixtures. To test the accuracy of determination of the amounts of the compounds, a third reference compound spectrum (basic-$PbCO_3$) was used in the calculations. This component was erroneously found to be contained in amounts of max. 5 % of the total lead content. The relative amounts of PbO and $PbCO_3$ could be calculated with a maximum error of ±5 % of the total lead content.

Fig. 2 shows the Extended X-Ray Absorption Fine Structure (EXAFS) spectrum of a lead-contaminated soil and the linear combination of 25 % $PbCO_3$, 37 % basic $PbCO_3$ and 38 % $PbSO_4$. The two spectra show a high degree of conformity. Remaining differences probably result from small amounts of additional not yet identified lead-compounds.

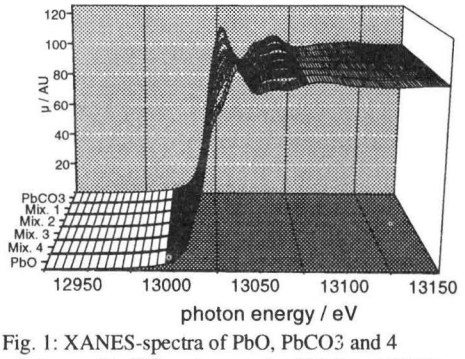


Fig. 1: XANES-spectra of PbO, PbCO3 and 4 mixtures with different amounts of PbO and $PbCO_3$

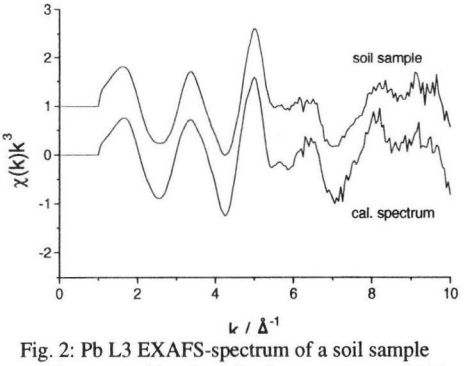


Fig. 2: Pb L3 EXAFS-spectrum of a soil sample and linear combination of reference spectra, 25 % PbO, 37 % basic PbCO3, 38 % PbSO4

The SEM/EDX investigations showed that the soil contained almost all lead in particulate form. They could be easily identified in the Backscattered Electron Detector (BSD) Images as bright particles. EDX analyses of these particles showed the Pb *M*, O *K*, C *K* and probably S *K* peaks. The S *K* peak is overlaid by the Pb M peak but can be identified through the deformation of the sum peak.

The presented results show, that it is possible to identify heavy metal compounds in soils by XANES/EXAFS-spectroscopy. Remaining differences between the linear combinations of reference spectra will be minimised, when additional reference spectra are available. The detection limit which was in the order of 50 g/kg of the respective heavy metal can be improved by a factor of 100 by using the fluorescence technique

References

[1] Calmano W. (1989) *Schwermetalle in kontaminierten Feststoffen*, Verlag TÜV Rheinland, Köln

[2] Manceau A. et al. (1996) Direct Determination of Lead Speciation in contaminated Soils by EXAFS Spectroscopy *Environ. Sci. Technol.* 30, 1540-1552

Influence of Organic Pollutants on Sorption of Naphthalene in Contaminated Soils.

by
Rémy M. Bayard, Ligia Barna, and Rémy Gourdon.*

LAEPSI, Laboratoire d'Analyse Environnementale des Procédés et des Systèmes Industriels, INSA Lyon, Villeurbanne, Rhône, 69621, France.

(*) Corresponding Author:
Dr. Rémy Gourdon
INSA Lyon
LAEPSI, Bat. 404.
Villeurbanne, 69621 Cedex, (France)
Fax. 33-4-72-43-87-17
Email. Gourdon@insa.insa-lyon.fr

Keywords: Behaviour of contaminant, Contaminated soil, Mobility, Naphthalene, PAHs, Soil contamination, Sorption, Transport in soil, Xenobiotic.

Development of in-situ clean up treatment of polluted sites needs a better understanding of the mechanism which control the transfer of soluble organic pollutants. Generally, spreading of spillage materials is assumed to be primarily controlled by sorption of organic pollutants on Soil Organic Matter (SOM). Partition mechanisms between Xenobiotic Organic Matter (XOM) and leachable organic pollutants have not yet been fully studied. In this work, both batch and column experiments were used to study the effects of the Polynuclear Aromatic Hydrocarbons (PAHS) on the sorption and transport of naphthalene in soils. Initially, batch tests were carried out in order to study the effect of coal tar particles on the sorption equilibrium of naphthalene using Fontainebleau sand and a selected organic soil (CSAC) as matrices. Coal tar was obtained from a highly polluted soil from a manufactured gas plant site. In a second stage, the column experiments were conducted on the two matrices either in presence of coal tar particles or not.

PAHs in solution have no effect on naphthalene sorption equilibrium, due to the low solubility of the pollutants which makes competition unsignificant. Sorbed phenanthrene reduces naphthalene adsorption only when present at relatively high concentration (about 100 mg.kg-1) in the soil. In contrast, experiments carried out in the presence of coal tar, either artificially added to a virgin soil or sand or already present in a real contaminated soil, showed a significant effect on the retention behaviour of naphthalene. Naphthalene retention was found to be directly proportional to the amount of coal tar added to the sand or soil (Figure 1). A better affinity of naphthalene for coal tar than natural organic matter of the soil was observed.

Solid-liquid partition during transport in column experiments was very well modelled with a double compartments model for the two interactive materials (SOM and XOM). For natural Soil Organic Matter (SOM), the model considers a surface (with instantaneous sorption) and internal compartment (with a rate limited sorption) for SOM. In the presence of coal tar particles into the CSAC soil, XOM was considered as

a second internal compartment with a specific rate limited sorption. The model parameters have been separately adjusted with pure CSAC soil and Fontainebleau sand columns spiked with coal tar particles (Figure 2). In the latter case, result showed that 90% of the "sorption site are located inside the coal tar particles. The retention mechanism can be possibly explained in terms of the dissolution and diffusion of naphthalene into the tar.

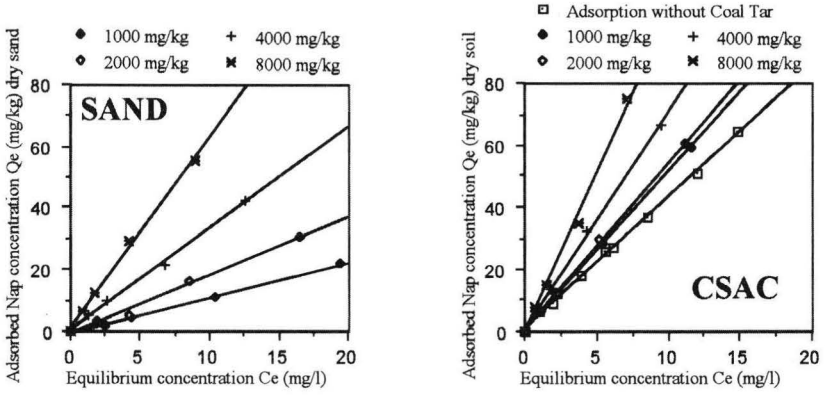


Figure 1. *Naphthalene sorption on Fontainebleau sand and CSAC in the presence of coal tar particles at different concentrations.*

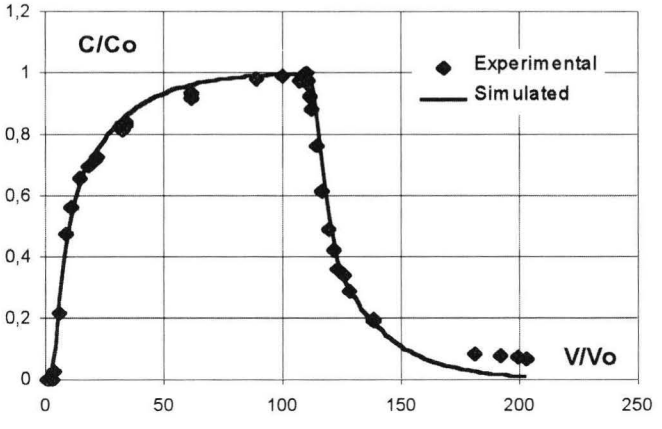


Figure 2. *Comparison of double compartment model simulations for XOM and SOM experimental data obtained during naphthalene transfer through sterilized CSAC soil column in the presence of coal tar particles (4000 mg.kg-1 of dry soil, diam. of particles < 1mm).*

Reference:

Bayard, R. Etude de l'Adsorption / Désorption de Polluants Organiques dans les Sols. Approche Méthodologique et Application au Pentachlorophénol et aux Hydrocarbures Aromatiques Polycycliques. Thèse de Doctorat. INSA Lyon, 1997, 231 p.

LONG TERM METAL RELEASE FROM DEPOSITS OF MUNICIPAL SOLID WASTE INCINERATION (MSWI) BOTTOM ASH

Günther Hirschmann & Ulrich Förstner

Technical University of Hamburg-Harburg, Section of Environmental Science and Engineering, P. O. BOX 901052, D-21073 Hamburg, Germany

Key words: Stabilized waste, incineration, atmospheric deposition, leaching behaviour, heavy metals, buffering capacity, environmental risks

1. INTRODUCTION

The German regulation for waste deposits, the so called „TA Siedlungsabfall", excludes all waste from disposal, which has a total organic carbon content (TOC) of more than 3 or 5 weight percent, depending on the disposal standard. The reason is to prevent biochemical reactions in the landfill. As a consequence the waste must be treated prior to disposal mainly by incineration. Although there is a long tradition of bottom ash utilization in low grade construction applications the long term behaviour is not very well known yet.

2. LONG TERM BEHAVIOUR

The main aspect for the long term behaviour of waste within a geological time scale is the release of contaminants. For an assessment of the future emissions the release mechanisms and the transport mechanism like advection or diffusion must be known. But also geochemical driving processes have at least the same significance. They are caused by chemical gradients of pH-, redox-conditions, concentration of organic ligands and salts between the waste-matrix and the environment. The geochemical driving processes in combination with the capacity controlling properties of the waste matrix (exchange-, sorption- or buffer capacities) cause the resulting chemical environment, which often change in time.

On the one hand capacity controlling properties like acid producing processes (sulphide oxidation or organic matter decay) can force changes of the chemical environment for example pH-decrease. On the other hand acid neutralization capacity (mainly caused by carbonate content) slows down the pH-change. If the pH decreases the main question is: does the metal release will take place suddenly and strongly at a specific pH-level (chemical time bomb) or slowly and compatible with the environment.

3. GEOCHEMICAL AND MINERALOGICAL CHARACTERIZATION

Burning the waste at temperatures between 850 and 1000°C produces the bottom ash which is quenched by water and afterwards processed by sieving, separation of metals and storing for 3 months. After contact with water and air several chemical reactions like hydration, oxidation and carbonatization start and produce heat as well as hydrogen gas. Storing under wet conditions for 3 months allows these reactions to occur prior to utilization or disposal. For our investigations we used only stored bottom ash.

Chemical bulk analyses show a high content of salts (chloride and sulphate) and heavy metals, especially chromium, copper, lead and zinc compared to geological material. There is still an TOC content of 0,8-1,5 wt.-% because of insufficient burnout. In contact with water the bottom ash shows an alkaline pH between 10 and 11. The acid neutralization capacity to pH 4 (ANC_4) is about 1,5 meq protons/g dry matter.

Contaminated Soil '98, Thomas Telford, London, 1998, 851–853

As main phases we found silicatic glass (40-50 vol.-%), quartz (6-10 vol.-%), other crystalline silicates like pyroxene, olivine or melilite (2-23 vol.-%), magnetite/other ironoxides (3 vol.-%), elemental metals/Si-Al-Fe-alloys (1-4 vol.-%) and a very fine grained matrix (3 vol.-%). The porosity varies between 4 and 35 vol.-%. The heavy metals are mainly bound in alloys (Cu, Zn, Ni, Pb), spinells (Cr, Pb), glas (Zn, Pb) and some silicates eg. melilite (Zn) or pyroxene (Cr).

4. LABORATORY LYSIMETER TESTS

Leaching tests are normally used to investigate the contaminant release (IAWG, 1994). However, the transfer of batch leaching test results into field conditions will pose problems because of several processes which can not be realized by batch tests. These are:

- kinetic effects especially acid buffering by silicates,
- the formation of secondary phases like iron oxides or clay minerals, which can incorporate or sorb metals,
- the decay of organic matter, which can lower the pH and complex metals,
- the development of redox conditions and
- the metal release pattern with time.

That`s why we conducted several laboratory lysimeter tests, which have been run with water for one year or acidified water (pH-controlled) for some months.The leachates of the lysimeters without pH control show a nearly constant pH of 11 and an increasing redox potential from slightly reduced to oxidized conditions. The soluble salts and organic compounds are released very quickly with increasing liquid/solid-ratio. The calcium leaching at high pH-values about 10 is limited by the solubility of gypsum. Although the supply of carbondioxide is limited in saturated flow conditions, precipitation of calcite and therefore increase of the ANC_4 (by max. 30%) takes place. The metal content of the leachates in general is very low.

The leachates of the pH-controlled lysimeters reached pH 4 after 5 or 6 months and show 3 buffering plateaus. A small one can be seen at pH 9,5 and a strong one between pH 7 and 5,5. Below pH 5 the pH again decreases very slowly. The release patterns of calcium and carbonate clearly show, that dissolution of calcium carbonate is mainly responsible for the buffering zone between pH 7 and 5,5. Other calcium phases like calcium silicate hydrates buffer the added acid at pH 9,5, aluminium and iron oxides/hydroxides in addition to silicates are responsible for buffering at pH-values below 5. The heavy metal release pattern of the pH-controlled lysimeters are similar to each other. Zinc, nickel, copper and partly cadmium are released first between pH 7 and 5,5 in the carbonate buffering zone (mainly Zn) and a second time at pH values below 5 (mainly Cu; Figure 1). Lead is significantly released only at pH values below 5. The chromium concentrations of all leachates were independent of pH and have always been found to be less than 0,01 mg/L. In relation to the total metal content 49 wt.-% Cd, 5 wt.-% Cu, less than 0,5 wt.-% Cr, 11 wt.-% Ni, 3 wt.-% Pb and 18 wt.-% Zn were released.

Compared to the pH_4 static batch test with bottom ash powder the metal release during the pH-controlled lysimeter test with original bottom ash is in the same order of magnitude. Not pulverized bottom ash however shows much less metal release during the batch test. For an assessment of long term metal release by short period batch tests the bottom ash has to be pulverized.

A pH_4 static batch test with the powder of the pH controlled lysimeter ash showed, that there is still a considerable release potential for some metals. The total metal release of the lysimeter treated bottom ash (lysimeter test and batch test after grinding) is often higher than the release of the untreated bottom ash powder in the batch test. Changing

of metal binding forms during the lysimeter test and kinetic effects seem to be responsible for this development.

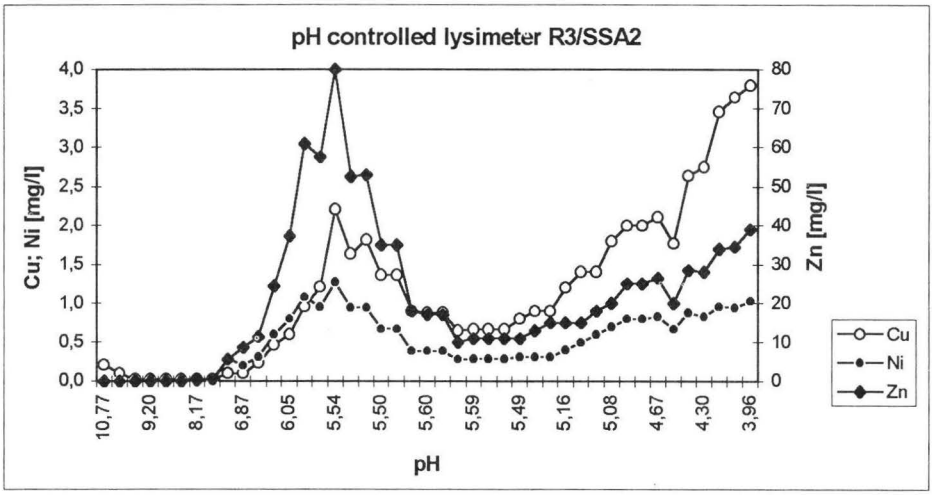


Figure 1: Concentrations of Cu, Ni and Zn related to pH in the leachate of the pH-controlled lysimeter.

Mineralogical investigations of the leached bottom ash showed, that mainly alloys were destroyed even in the ashes which were leached by water only. Secondary phases like metal oxides/hydroxides (mainly iron phases) and crusts of amorphous, water bearing Al-Si-oxides were formed.

5. LONG TERM BEHAVIOUR OF BOTTOM ASH MONOFILLS

To avoid heat as well as hydrogen-gas production and to force carbonatization bottom ash has to be stored for 3 months prior to disposal.

The metal release is controlled by the pH-development. Internal acid producing processes like decay of organic matter or oxidation of sulphides are not an important factor for the pH-decrease. The acid neutralization capacity is mainly reduced by the environmental acid input in connection with the release of buffering phases (mainly calcite). The newly formed phases like carbonates or hydroxides are responsible for the quick metal release of Zn, Ni, Cu and partly Cd during the carbonate buffering zone. The metal release starts at about pH 7. Pb and Cu are released at pH 5. Cr is bound in iron hydroxides or spinells and released only at pH <4. Depending on the environmental conditions (water balance, acid rain) and landfill design (compaction, permeability, cover, thickness) it can take hundreds till thousands of years until metal release starts. The long term metal release can be assessed only by pH static batch tests with pulverized bottom ash.

IAWG: INTERNATIONAL ASH WORKING GROUP (1994): An international perspective on characterization and management of residues from municipal solid waste incineration. Summary Report, 77 p.

This research project was supported by the German Ministry for Education, Science, Research and Technology (FKZ1460799A).

Managing C/N Ratios in Horse Manure Utilization Systems

Randall E. James, Ph.D.

The Ohio State University, P.O. Box 387, Burton, Ohio 44021, USA

Key words: ammonia, carbon balance, fertilization, immobilization, manure, nitrate, nitrogen, prevention.

Wood sawdust is one of the most common bedding materials used for horses. The high C/N ratio in horse manure and hardwood sawdust mixtures can induce a nitrogen deficiency in growing crops, due to the immobilization of soil nitrogen by microorganisms as they break down this material. Mixtures of hardwood sawdust plus horse manure were added to 500 ml plastic cartons. Various rates of urea and ammonium nitrate were added to the mixtures to produce a range of C/N ratios of 80:1 to 30:1. The treatments were incubated at 25°C for 10-12 weeks, and monitored for changes in C/N ratio. The treatments with the largest urea applications, and therefore the narrowest C/N ratios at the beginning of the incubation period, had the widest C/N ratio at week 2, significantly wider than the treatments where little or no urea was applied. Throughout the incubation period, the horse manure plus hardwood sawdust plus ammonium nitrate treatments maintained a significantly narrower C/N ratio than the horse manure plus hardwood sawdust treatment where no ammonium nitrate was added.

A greenhouse study was also conducted using a Typic Hapludalf (Chili loam) soil and various horse manure plus hardwood sawdust plus ammonium nitrate mixtures. The mixtures were used fresh and after composting, and were screened for possible phytotoxic effects. No phytotoxic effects were observed. Pots with annual ryegrass (*Lolium multiflorum*) were maintained in a greenhouse for six weeks. The ryegrass in all of the treatments where ammonium nitrate had been added took up significantly higher amounts of nitrogen than the control (soil only). The ryegrass in the horse manure plus hardwood sawdust treatments without ammonium nitrate took up significantly less nitrogen than the control, indicating an induced nitrogen limitation and net nitrogen immobilization in the soil.

Evidence collected in these studies strongly suggest that horse manure plus hardwood sawdust bedding, as it is removed from a stable, is not acid enough to convert NH_3 to NH^+_4 as urea is hydrolyzed. NH_3 is therefore volatilized, passing through and eventually out of the collected horse manure plus hardwood sawdust mixture. This is the only plausible explanation for the increased C/N ratio observed when these materials were incubated in the presence of urea. Volatilizing NH_3 is toxic and would tend to suppress the heterotrophic microorganisms which break down organic materials.

Ammonium nitrate was effective in reducing the initial C/N ratio of manure/bedding mixtures collected from stables. Unlike urea, ammonium nitrate was retained in the system and maintained a C/N ratio low enough to prevent immobilization of soil nitrogen regardless of the length of storage. The addition of ammonium nitrate to horse manure plus hardwood sawdust mixtures provided a "low-tech" solution to a problematic agricultural waste. Stable owners could simply add approximately 150g ammonium nitrate/horse/day to the manure and bedding as it is being cleaned out of the stall. Additional handling of the manure would serve to further mix the ammonium nitrate. Once the ammonium nitrate was added the manure and

bedding mixture would be immediately fit for use on crop producing soil. It could also be stored for later use. This simple process quickly and economically transforms an agricultural waste material, which will reduce crop yields, into a manageable nutrient source to be utilized for crop production.

SOLID-LIQUID PARTITIONING OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH) IN COLUMN EXPERIMENTS ON HARBOUR SLUDGE

Th.J.S. Keijzer, P.F. Middeldorp, M. van Alphen and J.P.G. Loch

Utrecht University, Department of Geochemistry, P O box 80021, NL-3508TA Utrecht, The Netherlands.
tel: +31 30 2535045, fax: +31 30 2535030, keijzer@earth.ruu.nl

KEYWORDS
desorption, partitioning, polycyclic aromatic hydrocarbons, sludge

SUMMARY
Partition coefficients for six PAH were determined on harbour sludge in column experiments under non-equilibrium conditions. The K_p^{app}-values show significant differences from those obtained under equilibrium conditions, especially for the heavier, hydrophobic compounds. Removal of the lighter PAH can be modelled with a spherical and semi-finite diffussion model for the first pore volumes. However, with increasing number of displaced pore volumes the non-equilibrium conditions for these compounds also increases.

INTRODUCTION

Sorption of organic molecules like polycyclic aromatic hydrocarbons (PAH) involves partitioning of these compounds between the solid and liquid phase, described by the equilibrium partition coefficient K_p. Because of the association of PAH with dissolved organic matter (DOC) and colloids in the aqueous solution an apparent concentration, c_w', in the water phase exists. Consequently an apparent partition coefficient, K_p^{app}, is often reported in the literature. Most K_p^{app}-values are determined using batch experiments conducted over a short period of time, typically 48 hrs. However, laboratory and model studies indicate that for PAH the time needed to reach equilibrium can exceed one month. K_p^{app}-values obtained from batch adsorption experiments are thus under-estimated (Ball & Roberts, 1991; Wijdeveld, 1994), in desorption experiments they would presumably be over-estimated. In column experiments, which may be a more realistic representation of the natural situation, asymmetrical breakthrough curves and extended tailing due to the continued renewal of porewater and thus non-equilibrium were observed Gratwohl *et al.*, 1993; Brusseau *et al.*, 1991).
The objective of this study was to determine the desorption behaviour of PAH in contaminated harbour sludge in laboratory column experiments subjected to a hydraulic pressure gradient.

EXPERIMENTAL

Two harbour sludge samples were retrieved from the "Beerkanaal" (BK) and "Beneden Merwede" river (BMR) in the Port of Rotterdam, the Netherlands. Both sediments are heavily contaminated with PAH. The PAH under investigation in this study were phenantrene (Phe), antracene (Ant), fluoranthene (Flu), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF) and benzo[a]pyrene (BaP). Glas columns were packed with a mixture of harbour sludge and sand. Of each sludge sample two columns were packed and percolated. The eluate was collected and analysed weekly for PAH, DOC and Cl^-. The columns were kept at a constant temperature of 277K, under dark, anaerobic conditions to minimise degradation of PAH. The PAH concentrations in the eluate were determined on a Hewlett-Packard model 1050 HPLC, equipped with a Bakerbond 5PAH reverse-phase column and a fluorescence detector.

RESULTS AND DISCUSSION

Figure 1 shows the development of the concentration of Phe, Ant and Flu in the column eluate for one of the columns packed with BMR sludge. Concentrations in the effluent decreased rather steadily during the experiment, indicating that the desorption of the PAH is a relatively fast process. A decrease in DOC from 60 to less than 1 mg L^{-1} resulted in a less than proportional decrease of the PAH concentration in the eluate. From the c_w' values at the end of the experiment and the total PAH content of the samples K_p^{app}-values were determined (Tabel 1). In Table 1 values obtained from stored batch samples are also listed, these were retrieved in 1993 from the same locations and stored at 277K and only recently analysed for PAH. It is assumed that the PAH concentrations in these samples represent equilibrium conditions. There is a good agreement between the column duplicates, but values obtained for percolation experiments are higher than those obtained for the stored batch samples and values obtained from batch experiments on comparable harbour sludge from the Port of Amsterdam (Wijdeveld, 1994). The deviation from equilibrium increases with decreasing water solubility. Hydrophobic compounds require longer equilibrium times

than the more hydrophilic compounds (Grathwohl *et al.*, 1994). Elution of the lighter compounds (Figure 2) can be modelled reasonably well for the first two pore volumes with a semi-finite model with radial diffusion from spherical particles. However, with progressive pore volumes the elution also becomes non-lineair.

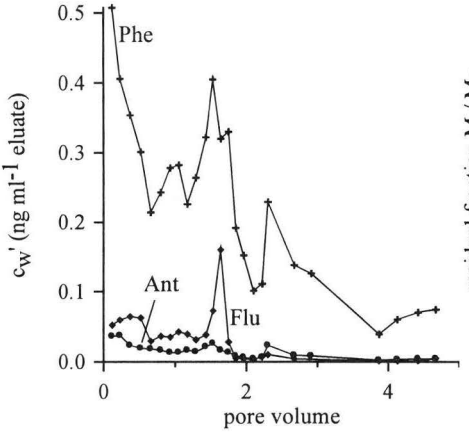


Figure 1 Concentration in the effluent for three of the PAH in a column with BMR.

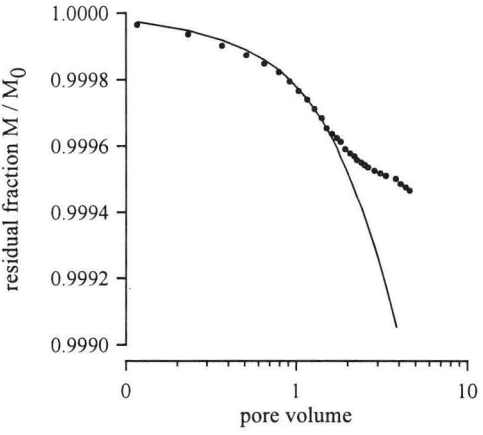


Figure 2 Desorption of Phe from a column with BMR, symbols are measured, line is calculated using Grathwohl *et al.* (1994).

compound	Log K_p^{app}				
	BMR column	BMR batch	BK column	BK batch	Wijdeveld (1994)
Phe	3.59 ± 0.09	3.79	3.57 ± 0.02	3.28	not analysed
Ant	4.63 ± 0.12	4.30	4.32 ± 0.01	3.98	3.15
Flu	4.49 ± 0.17	4.11	4.44 ± 0.09	4.07	3.60
BbF	5.52 ± 0.28	4.40	5.00 ± 0.01	4.50	3.79
BkF	5.47 ± 0.08	4.46	4.88 ± 0.04	4.46	3.72
BaP	5.60 ± 0.08	4.49	4.89 ± 0.01	4.30	3.81

Table 1 K_p^{app}-values for the different PAH from the column experiments, stored batch samples and values obtained from batch experiments by Wijdeveld (1994).

We conclude that K_p^{app}-values obtained from column experiments give a more realistic value for the elution of PAH in sediments subjected to advective water transport than those obtained by batch experiments. Removal is slower than calculated with a diffusion limited model.

REFERENCES

- Ball WP & Roberts PV (1991), *Environ. Sci. Technol.*, **25**, 1239-1249
- Wijdeveld AJ (1994), MSc-thesis, University of Utrecht, the Netherlands
- Grathwohl P, Gewald T, Pyka W & Schüth C (1993), **Contaminated Soil '93** (Arendt et al eds.), Kluwer Acedemic Publishers, Dordrecht, 175-184.
- Brusseau ML, Jessup RE & Rao PS (1991), *Environ Sci. Technol.*, **25**, 134-142
- Grathwohl P, Pyka W & Merkel, P (1994), **Transport and reactive processes in aquifers** (Dracos & Stauffer, eds.), Balkema, Rotterdam, 469-474

ESTIMATION OF BIAS IN THE MEASUREMENT OF 'HOT SPOTS' ON CONTAMINATED LAND

Sharon Squire[1], Michael H. Ramsey[1] and Michael J. Gardner[2]

1 Environmental Geochemistry Research Group, T. H. Huxley School of Environment, Earth Science and Engineering, Imperial College of Science, Technology and Medicine, London, UK, SW7 2BP
2 WRc plc, Henley Road, Medmenham, Marlow, Bucks, UK, SL7 2HD

Key Words: contaminated soil, samples, quality control.

SUMMARY
A synthetic sampling target has been constructed for the estimation of sampling bias and the estimation of measurement uncertainty, using inter-organisational sampling trials. The approach provides realistic estimates of uncertainty whatever sampling protocol is applied, which is in contrast to the idea of assuming that a 'correct' sampling protocol will give a representative, and unbiased sample. As this investigation is still in progress the complete results are not yet available.

INTRODUCTION

A common requirement in contaminated land surveys is to spatially delineate the most contaminated areas to facilitate either remediation or development. Methods for estimating sampling bias are being investigated using an inter-organisational sampling trial upon a sampling target with synthetic hot spots, in Ascot, UK. The sampling target has been developed by adapting the analytical method of 'spike recovery' used to estimate analytical bias. As such, this site has advantages over previous sites for which consensus values between participants were used to estimate bias in sampling when determining the mean contaminant concentration at the site (Ramsey, *et. al.*, 1995). The objectives for each participant in the present sampling trial were to: (a) estimate spatial bias in the location of synthetic 'hot spots' within the sampling target, and (b) determine the bias in the estimated concentration of the analyte, using spike recovery.

EXPERIMENTAL

A 30m by 30m sampling target has been constructed at a greenfield site by spiking the top 15cm of soil with barium sulphate, thereby creating synthetic hot spots of known position, dimension and concentration. Four methods, described below, have been carried out by samplers from 5 universities and 4 commercial organisations to determine measurement uncertainty (Ramsey and Argyraki, 1997). The four methods carried out were, (1) single sampler/single protocol (2) single sampler/multiple protocol (3) multiple sampler/single protocol (i.e. a collaborative trial in sampling - CTS) and (4) multiple sampler/multiple protocol (sampling proficiency test - SPT). By using a synthetic sampling target, Method 1 is the most economic way of estimating sampling bias for a single protocol. This has been achieved by identifying the difference between the results obtained from the chemical analysis of the samples from one protocol and the assigned value of the synthetic sampling target. Method 2 compares the bias between different protocols. Method 3 shows the agreement between participant's results when they are using the same nominal protocol. It can also be used to show the 'fitness-for-purpose' of that specified protocol at the site. Method 4

provides (a) a realistic estimate of uncertainty of measurements in terms of both concentration and the position of contamination, for different protocols (that have been selected on the basis of professional judgement) and (b) an estimate of the performance of the sampler. The sampling precision for all protocols was calculated by taking duplicate samples at a distance representative of the expected spatial precision of the survey equipment used.

All sampling proficiency test and collaborative trial samples were analysed at Imperial College, UK to minimise the effect of analytical bias between participants. Soil samples were dried at 65°C, disaggregated in a pestle and mortar, and the <2mm portion ground to 75 microns. Analytical test portions of these samples were decomposed in nitric, perchloric and hydrofluoric acid and analysed by ICP-AES for barium. Analytical bias was estimated using 2 certified reference materials and 3 house reference materials, analysed in duplicate at random positions within each batch.

The best estimates of barium concentration at each sampling location were plotted on a base map, and a line drawn around the areas considered to be above a defined threshold. For the sampling proficiency test, the method for doing this was based on the participants professional judgement. For the collaborative trial in sampling a single method was used to allow comparability. The measured concentration and spatial characteristics of the hot spots determined by participants were compared against the known, or 'true' values. The results of each participant were scored on factors, shown schematically in Figure 1. These include, comparisons of the measured hot spot area (a_m) and true area (a_t); percentage of the measured hot spots covering the true hot spots (C); shape comparisons; and distance (d) between the centre of mass of the true (M_t) and measured (M_m) hot spots.

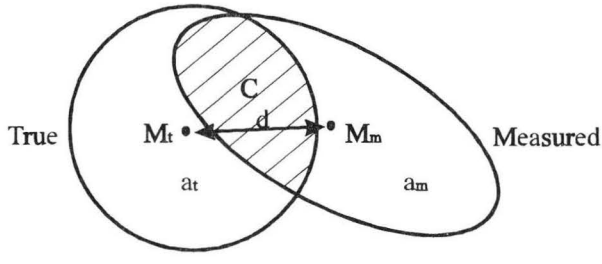


Figure 1

The uncertainty of all of these measurements is estimated from the variability between the participants, and therefore includes a component from sampling bias (Ramsey & Argyraki, 1997). Once sampling bias has been estimated, steps can be taken to reduce the bias and uncertainty, and thereby improve the reliability of land classification.

REFERENCES

Ramsey, M.H. and Argyraki, A. (1997). Estimation of measurement uncertainty from field sampling: implications for the classification of contaminated land, *The Science of the Total Environment*, **198**, 243-257.

Ramsey, M.H., Argyraki, A. and Thompson, M. (1995). Estimation of sampling bias between different sampling protocols on contaminated land, *Analyst*, **120**, 1353-1356.

Efficacy of Large Scale In-Situ Bioremediation Treatment of a BTEX contaminated Site regarding Dissolution and Degradation Kinetics

M. Meier-Löhr [1] , G. Battermann [1] , P. Werner [2]

[1] Technologieberatung Grundwasser und Umwelt GmbH, Maria Trost 3, 56070 Koblenz, Germany

[2] Institute for Waste Management and Contaminated Sites, Technical University of Dresden, 01796 Pirna, Germany

key words : in situ bioremediation, refinery site, aromatic hydrocarbons, BTEX, nitrate, carbon balance, mass transfer calculations, remediation efficiency

In situ bioremediation relies on stimulating the microbial activity and enhancing the mass transfer rate of contaminants from nonaqueous phase liquid (NAPL) phases into the aqueous phase. Mass balance calculations and hydraulic model approach are applied to assess the efficacy and kinetic constraints of a successfull large scale BTEX-remediation with nitrate as the predominant electron acceptor.

Based on laboratory tests, a pilot study and groundwater model calculations the large scale bioremediation system was designed for a groundwater flow of 400 m^3/h and an average residence time of 40 - 60 days in the subsurface treatment area (Battermann et al, 1993). Concerning dissolved aromatic hydrocarbons, iron and manganese ground-water clean up was required for reinfiltration. The hydraulic system of recovery wells and recharge trenches provided the delivery of nitrate (100-200 mg/l NO_3) and nutrients (5-10 mg/l PO_4) and the rise in groundwater temperature (+10° C).

Applying about 1000 metric tons (MT) of nitrate and 150 MT of oxygen during five years of operation the removal of hydrocarbons from nonaqueous phase liquid has been quantified of about 400 MT of hydrocarbons. About 80 % of the mass removal could be contributed to biological transformation and mineralization of hydrocarbons, evaluated from mass balances and adjusted stoichiometric relationships. Relevant compounds of mass balacing are the electron acceptors (NO_3^- , O_2, SO_4^{2-} , Fe(III), Mn (IV)), the inorganic carbon and alkalinity, the alkaline and alkaline-earth metals and the dissolved organic carbon. The contribution of mass balances to biological and geochemical reactions for quantification of hydrocarbon degradation has been evaluated by inverse modelling procedures (Meier-Löhr, 1998) adjusting „measured" and „calculated" mass balances of inorganic carbon and alkalinity.

The evaluation of multicomponent NAPL interphase transfer and biodegradation kinetics, has been carried out using an integral hydraulic modeling approach (Seagren et al, 1993). The mathematical model of the hydraulic system is based on an advection-dispersion-reaction equation incorporating a first-order mass-transfer relationship and first-order biodegradation kinetics for BTEX-compounds. According to the rise in groundwater temperature and groundwater

velocity an increase of the mass-transfer rate coefficients of about a factor of 2 from $3 \cdot 10^{-4}$ up to $6 \cdot 10^{-4}$ 1/d was calculated.

Based on the assumption that enhancement of NAPL dissolution caused by microbial activity relies on the increase in water solubility at interfaces a variable solubility factor was introduced. By model calibration it could be evaluated that the increase in NAPL dissolution by a factor of about 10 - 15 (compared with pumping measures) was mainly affected by the biological influence on hydrocarbon solubility in groundwater.

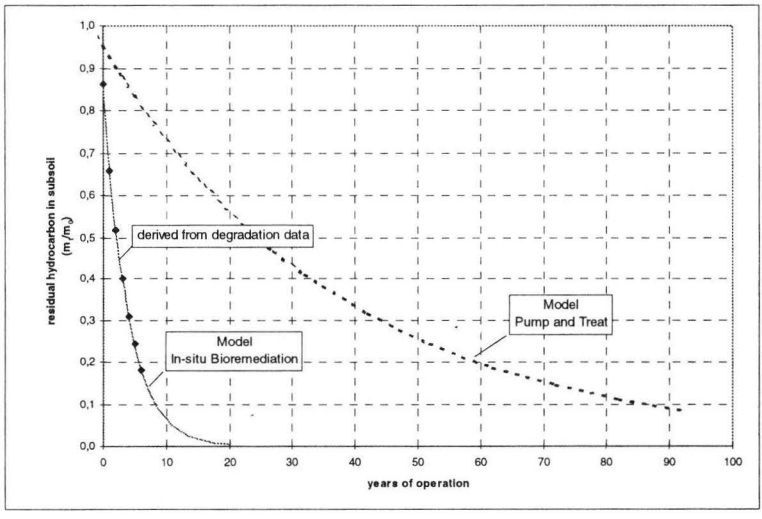


figure 1 : efficacy of in situ bioremediation treatment

In situ biodegration treatment applying nitrate as electron acceptor has been proven as an efficient technology to enhance the clean up of a BTEX contaminated site. The applied mass balance calculation, geochemical and hydrodynamic modelling methods give considerable support to bioremediation engineering and process control

References:

BATTERMANN, G., MEIER-LÖHR, M., WERNER, P. (1993) :Pilot and large scale experiences in the in situ bioremediation of a refinery site polluted with hydrocarbons, In: van den Brink, W.J., Bosman, R. and Arendt, F. (eds.) : *Contaminated Soil'93,* Kluwer Academic Publisher, Dordrecht pp. 1135 - 1444

MEIER-LÖHR, M. (1998): *Bilanzierung und Modellierung von biologischen und chem.-physik. Prozessen bei der In-Situ Sanierung von kohlenwasserstoff-verunreinigten Grundwassersystemen.*-Ph. D. Thesis Technical University of Dresden, Germany

SEAGREN, E.A., RITTMAN, B.E., VALOCCHI, A.J. (1993): Quantitative evaluation of flushing and biodegradation for enhancing in situ dissolution of nonaqueous-phase liquids.-*Journal of Contaminant Hydrology,* Vol 12, pp. 102-132

EFFECT OF METALS ON GROWTH OF FIELD-DERIVED SOIL BACTERIA.

Simone N. Mol[1], L.Anne Glover[2], Rolf D. Henkler[3] and Bruce N. Anderson[1]

1. RMIT University, Melbourne, Australia, 3000.
2. University of Aberdeen, Aberdeen AB25 2ZD, UK.
3. ICI Paints, Wexham Road, Slough SL2 5DS, UK.

Keywords: heavy metals, bioavailability, mercury, cadmium, chromium, copper, contaminated soil, microorganisms.

SUMMARY

Contaminated sites are frequently impacted by a variety of toxicants, including metals, hydrocarbons, and chlorinated solvents. The current study is an evaluation of the effects of metals on the growth on solid media of field-derived bacteria and is a component of a wider research program to examine the effects of heavy metals on the capacity of microorganisms to biodegrade hydrocarbons and chlorinated solvents. The bacteria used were isolated from an industrial site contaminated with solvent hydrocarbons without prior exposure to heavy metals.

METHOD

Extract bacteria from soil
(1% sodium pyrophosphate solution)
↓
Serial dilution and aliquots (0.1 mL) spread onto plate count agar (PCA). Incubated at room temperature for 7 days.
↓
Single colonies transferred to fresh agar plates according to a grid template.
↓
Plates incubated at room temperature for 7 days.
↓
Bacteria transferred to either PCA or mineral salts agar with the addition of either $HgCl_2$, $CdCl_2$, $CrCl_3$ or $CuCl_2$ at various concentrations (in triplicate).
↓
Incubated for 7 days at room temperature before plates were examined for growth.

RESULTS

Table 1. Growth on mineral salts citrate agar (% of total colonies exhibiting growth).

	Cadmium	Mercury	Copper	Chromium
0 mg/L	100	100	100	100
10 mg/L	96	91	92	100
20 mg/L	92	22	92	96
30 mg/L	88	44	92	100
40 mg/L	88	28	87.5	96
80 mg/L	88	20	87.5	92
160 mg/L	84	0	87.5	92

Table 2. Growth on plate count agar (% of total colonies exhibiting growth).

	Cadmium	Mercury	Copper	Chromium
0 mg/L	100	100	100	100
10 mg/L	77	81	100	100
20 mg/L	75	75	100	100
30 mg/L	63	69	100	100
40 mg/L	52	61	100	100
80 mg/L	32	7	85	94
160 mg/L	1	2	NP	1

Key: NP - not patched.

DISCUSSION

Growth was evident for 84% and 92% of strains propagated on mineral salts citrate agar in the presence of Cd and Cr, respectively, at 160 mg/L, but for only 1% of the strains propagated on PCA in the presence of Cd or Cr at 160 mg/L. The bacterial isolates appeared to be more adversely affected by metals when propagated on PCA rather than mineral salts media. Growth was evident for all isolates on PCA in the presence of either Cu or Cr up to 40 mg/L, whereas some isolates failed to grow in the presence of Hg or Cd at concentrations as low as 10 mg/L.

Previous studies by others have shown that components of growth media can bind heavy metal ions leading to variations in the apparent effect of the metals on target bacteria (Ramamoorthy & Kushner, 1975). Similarly, the binding of metals to subsurface soil components in the field can lead to variations in the apparent effect of metals on soil bacteria (Gadd, 1990). A determination of the true effect of metals on the growth of bacteria necessitates an understanding of the actual exposure (bioavailability) of the added metal to the target bacteria under the test conditions.

CONCLUSION

Our studies have shown that the growth of bacteria exposed to various metals in two laboratory media is quite variable, particularly at high metal concentrations, indicating that care should be taken with any interpretation of the effects of added metals in the absence of further information on the actual bioavailability of the added metals.

REFERENCES

Gadd, G.M. (1990) Metal tolerance. *In*: Edwards, C. Microbiology of extreme environments, Open University Press: Milton Keynes.

Ramamoorthy, S. and Kushner, D.J. (1975) Binding of mercuric and other heavy metal ions by microbial growth media. Microbial Ecology, 2:192-176.

TIME-BOMBS EFFECT IN AREAS OF THE CENTRAL RUSSIA WITH HIGH LEVEL OF RADIONUCLIDE CONTAMINATION OF SOILS

V. N. Golosov[1], N.N. Ivanova[1], A.V.Panin[2]

[1]Laboratory Soil Erosion and Fluvial Processes, Department of Geography, Moscow State University, Vorob'evy Gory, 119899, Moscow, Russia
[2]Branch of Geomorphology, Department of Geography, Moscow State University, Vorob'evy Gory, 119899, Moscow, Russia

Key words: inventory, isotope hydrology, soil erosion, sampling strategies, case study

SUMMARY
Vast areas of Europe were polluted after explosion on the Chernobyl nuclear power plant. The highest levels of contamination are observed in area around Chernobyl and some plots of the Central Russia in Tula, Kaluga, Orel and Kirsk regions. The main Chernobyl fallout ^{137}Cs is non-exchangeable (Davis, 1963) and has a very limited mobility by chemical processes. So physical processes associated with erosion, transport and deposition of sediment particles and with cultivation represent the major cause of ^{137}Cs redistribution in soils and of transfer of ^{137}Cs from soils to rivers and reservoirs (Owens et al, 1995). The features of caesium redistribution within typical landscapes of the Central Russia were studied in the Lapki balka basin (Tula region).

After detailed study of existing maps of Chernobyl fallout inventories for the region of the Central Russia, attention was focussed on the Plavsk region located about 250 km south of Moscow and more particularly the Lokna River basin. Chernobyl fallout inventories in this area were very high, with maximum level of up to 200 kBq m^{-2}. The Lapki balka basin with an area of 2,18 km^2 was selected for detail investigation. This area belongs to old-cultivated lands with period of intensive agriculture more than 350-400 years. The local black earth soils (chernozem) are extensively cultivated for cereals, maize, sugar beet, potatoes and perennial grasses. The tillage area is about 60-70% from total area. Intensive fieldwork programme was undertaken in the Lapki catchment. Activities involved included: 1.Collection of soil and sediment cores using 80mm and 68mm internal diameter core tubes. 2. Depth incremental sampling on the different element of relief within balka valley by excavation of 25x25 cm areas at 2-5 cm increments. 3. Measurement of ^{137}Cs activity in situ using a field-portable scintillation (NAI) detector . 4. Detailed topographic surveys of sampling areas and measurement points within the basin undertaken using a differential GPS. The data collected were used to produce 1: 2000 map and digital terrain model. Gamma-spectrometry analyses of soil and sediment samples were undertaken using HPGe detectors.

It is possible to determine initial spatial variability of ^{137}Cs within the Lapki balka catchment if to compare the ^{137}Cs inventory for flat watershed surfaces and uncultivated balka banks without sediment accumulation. The ^{137}Cs inventory slightly decrease from the north of the Lapki catchment from 450-470 kBq m^{-2} to the south till the 350-370 kBq m^{-2}. However for the centre part of catchment the initial inventory is likely the same as for the southern part. The erosion and accumulation processes are the main reasons of change concentration of ^{137}Cs in soils within basin. The annual soil erosion rates on cultivated slope at the Lapki catchment 4,6 t per ha. Most part

sediments from cultivated slope redeposit within uncultivated parts of balka banks and in the balka bottoms. The inventories on the uncultivated balka bank and on balka terrace can serve as a reference inventories (Table 1). The all other points are characterized the typical deposition surfaces. The maximum ^{137}Cs accumulation is observed in upper part of balka bottom because the concentrated flow from the slope sprawls here and lost its energy. There are no significant

Table 1. ^{137}Cs inventory of representative samples within the Lapki balka catchment

Location	Site	^{137}Cs (kBq m^{-2})
Uncultivated balka bank without deposition	23	376
Terrace at the balka bottom	14	416
Uncultivated balka bank with deposition	11	570
Upper reach of balka bottom	19	659
Middle reach of balka bottom	20	562
Middle reach of balka bottom	4	554
Middle reach of balka bottom	26	602
Lower reach of balka bottom	31	453

differences in ^{137}Cs level within the middle part of balka bottom (sites 4, 20, 26). Small increase is observed in site 26, which is located below nick-point in the balka bottom. At least very small increase relatively reference inventories is fixed in the lower reach of balka bottom, because of decrease in sediment concentration of flow and narrowing of balka bottom. This redistribution is confirmed by results of numerous bulk samples analysis. It is typical ^{137}Cs redistribution within small balka catchment of the Central Russia. Sediment budget calculations demonstrate that 90-95% of sediment redeposits within lower edges of cultivated field, uncultivated balka banks and mostly at the balka bottoms. The relationship between erosion and deposition areas is typically 10: 1accordingly. So the increase of ^{137}Cs in balka bottom due to sediment deposition exceed ^{137}Cs decay in 4-7 times.

Accumulation of large amounts of radionuclides on the balka bottoms and ponds presents a hazard of their possible immediate discharge into river channels with the flow due to a catastrophic storm. In this case, the failure of earth dams can have an avalanche-like character, which will significantly accelerate bed incision in balka bottoms, through which polluted deposits will be carried out into the rivers. The results of detail study of ^{137}Cs redistribution within small basin serve as a basis for forecast of ^{137}Cs contamination 40 years after the Chernobyl accident for the Plava basin and for the same landscapes as well.

Acknowledgements.
This work was supported by INTAS-RFBR grant 95-0734 and IAEA contract 9044.

References

Davis, J.J. (1963) Caesium and its relationship to potassium in ecology, in V. Shultz & A.W. Klement (eds) Radioecology, Jr. Rheihold, New York, pp.539-556.
Owens P.N., Walling, D.E. and He, Q. (1996) The behaviour of bomb-derived caesium-137 fallout in catchment soils, *J. Environment Radioactivity v.32, 3, 161-169.*

ONLINE MEASUREMENT AND SAMPLING QUALITY OF SOIL VAPOR

M. Nahold[1], J. Leest[2]

[1] G.U.T GRUPPE UMWELT+TECHNIK GMBH, Leonfeldnerstr. 18, A-4040 Linz, Austria

[2] Fresenius Umwelttechnik GmbH, Konrad-Adenauer-Str. 9-13, D-45699 Herten Germany

Key words: monitoring, monitoring procedures, sampling strategies, VOCs, chlorinated hydrocarbons, soil air, soil gas

Volatile organic compounds (VOCs) such as Perchloroethylene (PCE) or Trichloroethylene (TCE) as well as monoaromatic compounds find their way into the subsurface first by affecting unsaturated soil and then migrating into the groundwater. Natural and artificial inhomogeneities influence the results of measurements and sampling and reduce the efficiency of pneumatic in situ remediation.

The scale and extent of remedial measures are determined on the basis of the concentrations of VOCs in soil air samples. Therefore, the installation of monitoring wells, piezometers and various sampling devices are subject to ongoing discussion. There are various specific methods to sample or monitor soil vapors, and different approaches have been taken to standardize them. In other words, it is up to the investigator to choose the appropriate methods to obtain definite results. In Austria, the ÖNORM S2090 standard was established to guarantee a minimum quality level for sampling procedures. In Germany, the VDI 3865 standard has been published recently.

The inhomogeneity of the physical properties of the subground such as grain size distribution, soil moisture content and, consequently, permeability requires different monitoring probes and sampling techniques. High costs of analysis limit the number of samples, thus making it hardly possible to determine the reliability of the sampling procedure and the quality of the sample.

A gas measuring system developed recently by Fresenius Umwelttechnik GmbH was used for the measurements described below to detect Tetrachloroethylene. The compact self-calibrating 'airTOX Photometer' is based on an NDIR Photometer (Non Dispersive Infrared Absorption) that may be combined with different sensors. An infrared source produces broad band radiation that is led through a cuvette filled with the gas to be measured by means of a time-controlled aperture wheel. The gas-phase measured absorbs part of the radiation as a function of its concentration. The radiation emanating from the steel cuvette passes a narrow band filter before being measured by a detector.

The advantage of on-site measurements is illustrated by the example given in fig. 1, showing PCE concentration in the soil air monitored below a dry-cleaning shop. The soil gas samples were taken through a steel probe of a 10 mm diameter, with a filter screen located in sandy gravels 1.6-2.0 m below the surface.

The data set demonstrates that in this case it was possible to extract a comparatively large volume of soil air from a small diameter probe without any apparent influences from atmospheric air. When manual sampling started after the extraction of 50 liters, the concentration of PCE varied widely between 60 mg/m^3 and over 120 mg/m^3. Even more important than the absolutely true concentration of PCE in a sample is the information on the path of the concentration.

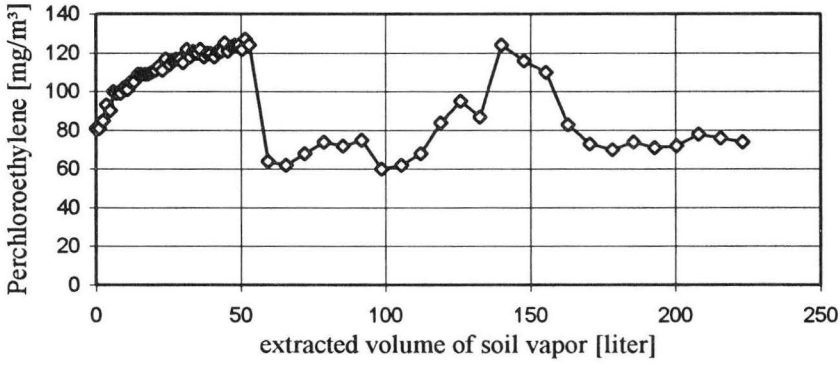


Figure 1 The concentration of PCE in soil air was monitored every 20 seconds over a period of 23 minutes. During the first 15 minutes a volume of 50 liters was sampled automatically at a rate of 3.75 l/min. Then the extracted volume was increased by additional manual sampling.

Sampling procedures may be controlled and properly evaluated by means of quantitative instrumentation helping to identify pneumatic interference immediately. As a consequence, the quality of both soil gas samples and documentation is improved. As a further option, soil vapor extractions may be surveyed and optimized automatically by means of a photometer installed on-site.

Soil vapor extraction (SVE) may be considered an established technology to remedy the unsaturated zone. Although case studies prove that the efficiency of SVE could be improved in nearly every case, only little progress was observed in practical application during the past five years. To investigate or survey a contaminated site properly, the concentrations of the contaminants have to be analyzed and piezometric heads have to be measured precisely. Online measurements of piezometric heads help to dimension SVEs. Surveys of piezometric heads also help to understand natural effects such as 'barometric pumping' in the unsaturated zone. The natural fluctuations of barometric pressure lead to a flow of soil air and, consequently, of contaminants. This effect might explain why tremendously varying concentrations of VOCs are observed in soil air at different times.

References:

ÖNORM S 2090 (1997) Sampling and analysis of soil-gas concerning volatile gaseous organic and inorganic compounds.

VDI 3865 Blatt 2 (1997) Measurement of organic soil pollutants, Part 2: Techniques of active sampling of soil gas.

ANALYSIS OF PAHs, HETERO-PAHs (N,S,O), AND N-SUBSTITUTED PAHs IN TAR OIL CONTAMINATED SOILS INCLUDING THEIR DEGRADATION PRODUCTS

S. Meyer, H. Steinhart

Institute of Biochemistry and Food Chemistry, University of Hamburg, Grindelallee 117, D-20146 Hamburg, Germany

Keywords: PAH, Hetero-PAH, metabolites, soil, analytical methods

Heteroaromatic compounds containing nitrogen, sulphur, or oxygen (PANH, PASH, PAOH) and N-substituted PAHs (cyano-PAHs, amino-PAHs) represent - with contents ranging from 5 to 13 % - a small but important part of coal tar oil [1]. As a result of the heteroatom these compounds are more polar than the analogous PAHs and therefore more mobile in the hydrogeologic environment. Moreover a number of studies have shown that nitrogen containing PAHs are important contributors to the mutagenicities of tar oils. Studies in culture media with tar oil adapted mixed bacteria culture have shown that NSO compounds can have a significant inhibiting effect on the biodegradation of many tar oil compounds [2].
To monitor PAHs and NSO compounds in tar oil contaminated soils and during biodegradation studies, analytical techniques had to be developed which reliably ensure the characterization of major and minor coal tar constituents over a wide concentration range as well as ensuring the identification and quantification of possibly hazardous intermediates. The determination of NSO compounds sets a high standard for the analytical scheme because of their wide polarity range, their different acid-base characteristics, the larger number of isomeric structures among the hetero-PAHs than among the PAHs in accord with the introduction of the heteroatom into the polycyclic ring-system.

The analytical method presented was developed on the basis of the established analytical schemes for characterization of mineral oil constituents and their metabolites [3,4]. PAHs, hetero-PAHs, and N-substituted PAHs were used as model compounds corresponding to typical tar oil compositions [1]. In addition PAH-metabolites previously identified in soil biodegradation studies [5] and hetero-PAH-metabolites from liquid culture media biodegradation studies were employed as model compounds. After a soxhlet extraction with dichloromethane a fractionation of the tar oil constituents and metabolites into 1. nonpolar PAHs, PASHs, and PAOHs; 2. neutral and basic polar compounds, and 3. acidic compounds is achieved by a solid phase extraction (SPE) over a combination of deactivated silica gel and an anion exchange material. Substances in fraction 2 are further separated into a neutral and a basic subfraction by their acid-base-characteristics using a cation exchange chromatography in SPE micro-columns (Fig. 1).

Applying the method to different tar oil contaminated soils (creosote contamination, gas work contamination) in addition to the typical tar oil PAHs a broad spectrum of isomeric heteroaromatic compounds and metabolites were identified on a mg/kg concentration level: Among the PASHs and PAOHs predominantly 3-ring and 4-ring compounds such as dibenzofurane, dibenzothiophene, benzo[b]naphthofuranes, benzo[b]naphthothiophenes

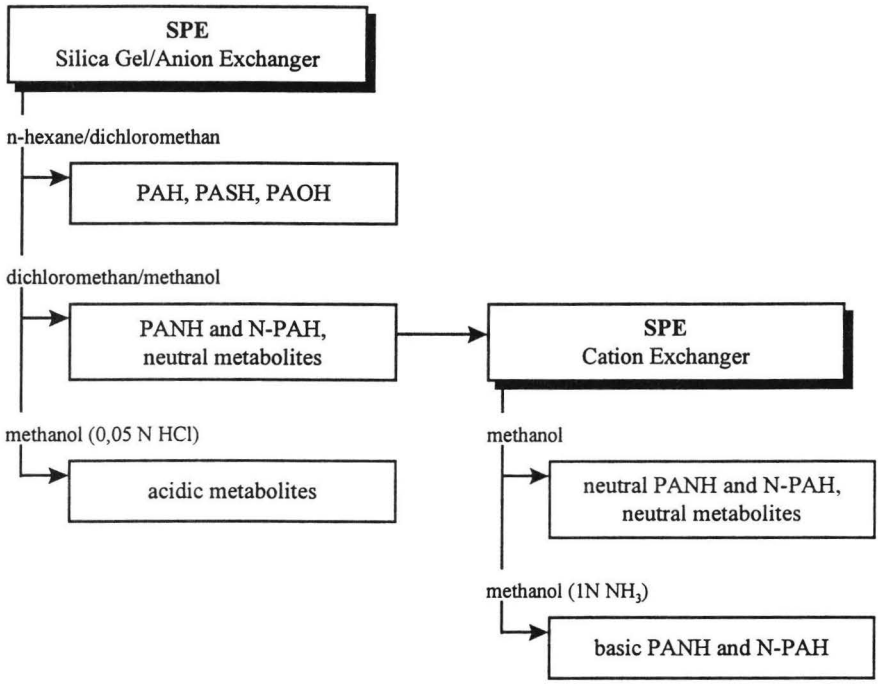


Fig. 1: fractionation scheme for tar oil constituents and their metabolites

and methylated derivatives were identified. The predominant part of peaks in the basic fractions were found to be basic 2-ring to 4-ring PANHs (azaarenes) such as quinoline, isoquinoline, acridine, phenanthridine, benzoquinolines, benzacridines, and their alkylated derivatives or amino-PAHs. The polar neutral fractions contained neutral 2- to 4-ring PANHs such as indole, carbazole, benzocarbazoles as well as some cyano-PAHs. In addition in this fraction PAH-metabolites such as 1-indanone, 9-fluorenol, 9-fluorenone, anthracene-9,10-dione, benz[de]anthracene-7-one, benz[a]anthracene-7,12-dione, and cyclopenta[def]phenanthrenone were identified. Identification and quantitative determination was carried out using reversed-phase HPLC with photodiode-array detection, and gas chromatography with mass-selective detection.

References

1. Collin, G. and Zander, M. (1985) Teer und Pech, in Ullmanns Enzyklopädie der Technischen Chemie, Vol. 22, Verlag Chemie, Weinheim, pp. 411-444.
2. Arcangeli, J.-P. and Arvin, E. (1995) Biodegradation rates of aromatic contaminants in biofilm reactors, *Wat. Sci. Technol., 31*, 117-128.
3. Langbehn, A. and Steinhart, H. (1994) Determination of organic acids and ketones in contaminated soils, *J. High Resolut. Chromatogr., 17*, 293-297.
4. Wischmann, H.; Steinhart, H.; Hupe, K.; Montresori, G. and Stegmann, R. (1996) Degradation of selected PAHs in soil/compost and identification of intermediates, *Intern. J. Environ. Anal. Chem., 64*, 247-255.
5. Wischmann, H. and Steinhart, H. (1997) The formation of PAH oxidation products in soils and soil compost mixture. *Chemosphere, 35*, 1681-1698.

DISTRIBUTION OF CR AND AS IN SOILS OF AN OLD TANNERY SITE AND IMPLICATIONS FOR FUTURE LAND USE

J. Gerth[1] and A. Leberer[2]

[1]Arbeitsbereich Umweltschutztechnik, Technische Universität Hamburg-Harburg, Eißendorfer Straße 40, D-21073 Hamburg; [2]Büro und Labor Dr. R. Wienberg, Gotenstraße 4, D-20097 Hamburg

Key words: arsenic, chromium, remediation, soil/plant transfer, soil washing,

SUMMARY

The decline of leather industry in central Europe in the late 1960's left behind hundreds of hectares of land contaminated with Cr and As as the major inorganic contaminants. Arsenic was used as As_2O_3 to preserve air-dried hides against microbial decomposition during transport from overseas. In the first half of this century As was also applied as As_2S_3 to assist as a reducing agent in the initial soaking and liming step of the production process. In the subsequent neutralization step As was washed off and discharged with the effluent. Chromium was the main tanning agent. When splitting and shaving the leather to uniform thicknesses fine leather particles were rubbed off and added to the effluent stream.

In this study, we investigated soils on an old tannery site and discuss procedures for their remediation. The total area of about 15 ha consists of former settling ponds (3 ha) and wastewater infiltration fields (12 ha) which were built on glaciofluvial sand about 4 m above groundwater level. The fields were last used in 1967. Since then terrestrial soils have formed with high contents of Cr and As beyond regulatory threshold values. Because of potential health risks the area has remained unused to this date.

The former settling ponds are covered with a 20-30 cm layer of sedimented waste consisting of leather particles and carbonate (organic carbon: 20 %, Ca-carbonate 40 %) with up to 1.3 % Cr and 100 mg/kg As. Chromium is exclusively bound to the leather particles and, for being immobile, is not found in the subsoil.

The topsoil of infiltration fields contains between 0.6 to 0.1 % Cr depending on the amount of sedimented solids. These formed a dense layer which had to be broken up mechanically when necessary in order to restore infiltration properties. By this action leather particles and Cr became distributed within the topsoil (Fig. 1). Arsenic is more mobile and present throughout the profile (0 - 2 m) in all soils and in different binding forms. The maximum concentration is normally found in the subsoil where As is closely bound to pedogenic iron oxihydroxides. Arsenic is also accumulated in the topsoil (Fig. 1) and is bound to organic matter as probably due to soil/plant transfer. This fraction has entered the nutrient cycle. The highest As content of >140 ppm was found in the Ah horizon of a cambic podsol in a separate area which was last used for wastewater discharge in the 1920's. In this case, deciduous trees (mainly oaks) have apparently depleted the subsoil and accumulated As on the surface with the leaf litter. Concentrations of more than 200 mg/kg arsenic were found in carbonate rich sediments of an irrigation ditch. Carbonate bound arsenic must be very immobile because the underlying iron oxide rich Bs horizon of a fossil podzol was not contaminated. Topsoils are also enriched with carbonate, N and S depending on the intensity of waste water irrigation. No hexavalent Cr was detected. Fractions of exchangeable or easy to mobilize Cr and As were not present or negligible, respectively.

Contaminated Soil '98, Thomas Telford, London, 1998, 873–874

Different remedial action techniques were tested in model experiments. Mechanical soil washing procedures to separate the highly contaminated leather particles from the siliceous soil matrix are not applicable. These particles are present as stable aggregates with 90 % > 0.063 mm and were not broken up even after intensive and prolonged stirring. Chemical soil washing is not effective either. By a 2-hour treatment of contaminated soil material using 0.01M HCl Cr was extracted 0.2 % and As 4.7 %. Selected areas of the infiltration fields could possibly be remediated by soil exchange against non-contaminated material. Chromium in the settling ponds could be removed by scraping off the leather particle/carbonate sediment layer. Deposition of contaminated material is only possible under non saturated and aerobic conditions. Arsenic, particularly in association with humic substances and iron oxihydroxides, is easily mobilized by reduction.

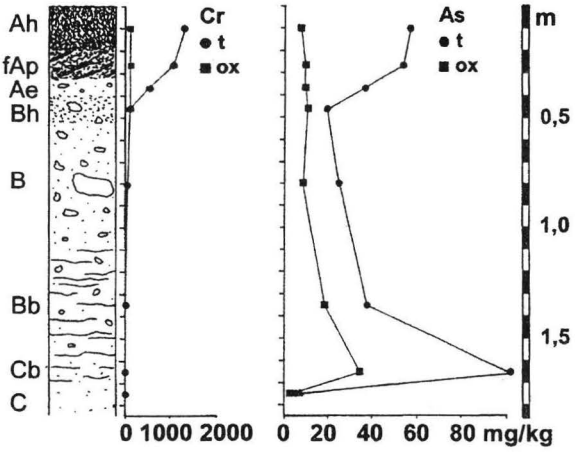


Figure 1 Depth profile of chromium and arsenic in an old tannery site infiltration field; t = total content as measured by aqua regia extraction; ox = oxalate soluble (0.2 M NH_4-oxalate, 4 hours in the dark); in the topsoil Cr is associated with fine leather particles while As is probably bound to humic substances. In the subsoil, the As content correlates with pedogenic iron (not shown).

For economic and also technical reasons, a remediation of the whole area by physical or chemical procedures is not possible. The results suggest that remediation concepts should include natural processes like the observed soil/plant transfer and accumulation of As on the surface. This process has to be investigated further in relation to appropriate plants, possible removal rates and the leaching of As in the vadose zone. A successful treatment would probably take several decades.

This research was part of the project 'Model risk assessment and remediation of old tannery sites' funded by the German Federal Ministry for Education, Science, Research and Technology (BMBF) and the City of Neumünster, Germany

SAMPLING CONTAMINATED SOIL: HOW MUCH SHOULD YOU TAKE HOME?

Rainer Bunge
EBERHARD Recycling AG, Schaffhauserstr. 61, 8302 Kloten, Switzerland

key words: contaminated site, contaminated soil, samples, sampling theories

Sampling in the field is generally carried out in blatant violation of the most fundamental principles of sampling theory. It seems that many sampling models are either too complex for practical purposes or, on the other hand, too simplistic to be used with confidence.
This is in particular true for the decision of the minimum sample mass to be drawn from a well mixed batch containing the contaminant in a highly accumulated form on distinct "carrier particles" (such as PAH carried by pieces of slag dispersed in the ground). We suggest as an acceptable trade off between simplicity and accuracy the following rule of thumb:

> Draw as much sample as necessary to recover at least 100 contaminated particles.

This statement can be derived by treating the sampling process by means of probability theory. For a start we assume that all particles in the material to be investigated have equal size (monodiperse material). Consider sampling a well mixed batch of this material containing N particles, of which X are contaminated ("carrier particles") and the remaining N-X are uncontaminated. A sample of n particles is drawn. How large must n be if the fraction of contaminated particles in the sample p=x/n is to lie within an acceptable range ε from P=N/X?
The outcome of this sort of "Bernoulli" experiment is described by the binomial distribution. Introducing reasonable assumptions it can be shown that the relative error for p is linked to the variable of the standardized normal distribution function, z, and the number of carrier particles contained in the sample, x, by the following equations:

$$\varepsilon = \left|\frac{p-P}{P}\right| = \left|\frac{x-nP}{nP}\right| = \frac{z}{\sqrt{nP}} \quad (1a) \qquad \left(\frac{z}{\varepsilon}\right)^2 = nP \approx x \quad (1b)$$

The acceptable relative error in sampling soils will generally be in the order of ε=20%. At a confidence level of 95% it follows that z=2. From equation 1b then follows that x=100 particles which corresponds with the above statement. Altogether n=x/p=100/p particles must be drawn for achieving the accuracy desired above.
For practical purposes it will be more useful to consider mass instead of the number of particles in a sample. If the carrier particles are assumed to be spheres of equal size, their mass fraction is:

$$C = \frac{c_t}{c_c} = \frac{m_c}{M} = \frac{x\pi\rho_c d_c^3}{6M} \quad (2)$$

C = mass fraction of carrier particles in batch
c_c = contaminant concentration in carrier particles
c_t = total contaminant concentration of the batch
M = total mass of the sample
m_c = total mass of carrier particles
ρ_c = density of carrier particles
d_c = diameter of a carrier particle

Using x = 100 particles for the accuracy chosen above and solving for M gives:

$$M \approx \frac{50 \rho_c d_c^3}{C} \qquad (3)$$

Note that the minimum sample mass depends on the size of the carrier particles and not on the size of the matrix material.

One can apply eq. 3 also to a size distributed material taking d_c as the maximum carrier particle diameter. In this manner, however, the necessary sample mass will be overestimated. Introducing a correction for size distributed carrier particles leads to the following expression:

$$M = \frac{1}{C}\left(\frac{z}{\varepsilon}\right)^2 \frac{\pi \rho_c}{6} \int_0^{d_{max}} d^3 f_3 \, d\,d = \frac{1}{C}\left(\frac{z}{\varepsilon}\right)^2 \frac{\pi \rho_c}{6} M^{(3)}(f_3) \qquad (4)$$

Here, f_3 is the density function of the size distribution and $M^{(3)}$ is the third moment. To solve this expression one must estimate the size distribution function of the contaminant carrier particles. Very often, carrier particles occur preferentially in the coarse size fractions. Their size distribution can therefore quite frequently be approximated by the GGS distribution. On log/log paper the cumulative form of this distribution gives a line with slope k.

$$F_3(d) = \left(\frac{d}{d_{max}}\right)^k \quad \text{with} \quad k = \frac{\log F_3(d_{max}) - \log F_3(d_{10})}{\log d_{max} - \log d_{10}} = \frac{1}{\log \frac{d_{max}}{d_{10}}} \qquad (5a,b)$$

The d_{10} is the mesh-width of the sieve that lets 10% of the feed pass and d_{max} is the maximum diameter of the contaminant carrier particles. The third moment of the GGS distribution is:

$$M^{(3)} = \frac{k}{3+k} d_{max}^3 = \frac{d_{max}^3}{1 + 3 \log \frac{d_{max}}{d_{10}}} \qquad (6)$$

Therefore the minimum mass of a sample should be:

$$M = \frac{1}{C}\left(\frac{z}{\varepsilon}\right)^2 \frac{\pi \rho_c}{6} \frac{1}{1 + 3 \log \frac{d_{max}}{d_{10}}} d_{max}^3 \qquad (7)$$

For typical cases of contaminated soils the minimum sample mass must be approximately:

$$M_{min} \approx \frac{10}{C} \rho_c d_{max}^3 \qquad (8)$$

Example

The target mound of a rifle range is to be sampled for lead content. We assume that the carrier particles contain 76% lead which gives c_c=76%. From preliminary investigations it is known that target mounds contain approximately c_t= 10'000 mg/kg = 1% lead. From eq. 2 follows that the mass fraction of bullet fragments in the target berm is C=1.31%. It is estimated that the maximum size of the carrier particles is given by the size of a standard bullet which is d_{max}=10 mm. Due to fragmentation on impact the bullet shreds are size distributed with a d_{10} of 0.1 mm. The density of a bullet is 10 g/cm^3. We accept an error of ε=20% at a 95% confidence level. From equation 7 follows that at least 5.7 kg sample must be drawn.

PHYSICAL REMEDIATION OF THE FINE SOIL FRACTION BY GRINDING ATTRITION

B. Schricker, Th. Neeße

Department for Environmental Process Engineering & Recycling, University of Erlangen-Nuremberg, Schottkystrasse 10, D-91058 Erlangen, Germany

Key words: environmental technology, fine particles, physico-chemical washing process, soil remediation, soil washing

INTRODUCTION

The decontamination of polluted soil or other mineral residues (eg sand-trap residues) by means of attrition is often either unsatisfactory or has no effect on particles sizes < 200 µm. The attrition process has now been improved and expanded on finer particles by adding small grinding media to the suspension, what results in a new process of grinding-attrition [1].

This process is carried out in agitation mills which are well known in comminution technique. Special installation units facilitate separation of the grinding media from the attrited soil fraction.

THE PRINCIPLE OF GRINDING-ATTRITION

Within the process of grinding-attrition, abrasion of the particle surfaces is caused by intensive shear and friction stresses between the agitated grinding balls. To avoid break-up of the soil particles, the size of the grinding elements should be chosen close to the maximum particle size. In the case of soil fractions < 150 µm, grinding elements with diameters of 200 µm lead to a high decontamination rate and after the process could be separated from the suspension without difficulty. Fig. 1 shows the principles of the grinding-attrition process. After grinding-attrition, the abraded, highly contaminated fine-fraction is separated from the cleaned coarse fraction by wet classification. The fine-fraction must then be disposed of or treated in a further process step.

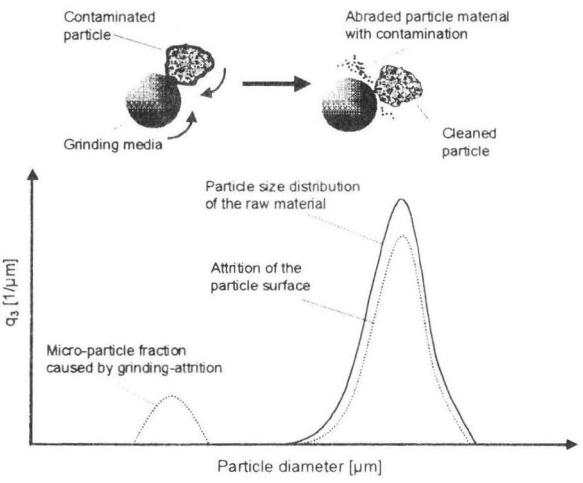


Fig. 1: Principle of the grinding-attrition process

Contaminated Soil '98, Thomas Telford, London, 1998, 877–878

GRINDING-ATTRITION AND ITS EFFECT ON REMEDIATION OF FINE SOIL FRACTIONS

In order to verify the advantages of the grinding-attrition process in fine soil remediation, lab-scale experiments were carried out with several mineral-oil contaminated sand fractions using both grinding-attrition and common attrition in a 5l-attritor.

As can be seen in Fig. 2, in the case of mineral-oil contaminated sand fraction 315 - 1000 µm, a higher decontamination rate can be realised using the grinding-attrition process than with common attrition (without use of grinding media). After grinding-attrition a decontamination rate of about 50 % can be achieved, producing about 10 % of contaminated fines (see Fig. 2, middle columns). In contrast, using the common attrition process a decontamination rate of only about 12 % and a production of contaminated fines of only 1 % was obtained (Fig. 2, left columns).

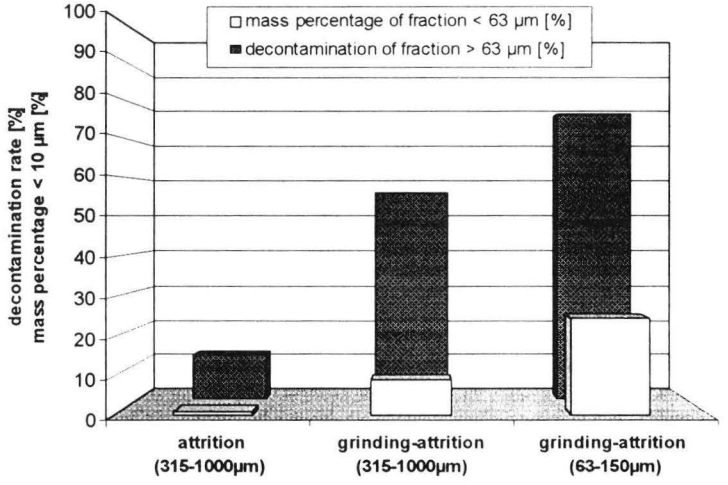


Fig. 2: Comparison of the decontamination of several mineral-oil contaminated residues using both common attrition and grinding-attrition

In order to investigate the efficiency of grinding-attrition in fine soil remediation, further experiments were carried out with an artificially contaminated sand fraction 63 - 150 µm. As shown in the right columns of Fig. 2, a decontamination rate of up to 80 % after grinding-attrition could be reached with a highly contaminated fine fraction < 10 µm production of about 20 %. In this particle size range common attrition showed no effect in decontamination and production of fines at all.

Further research is focused on optimization of the grinding-attrition process and on the transfer of the process industrial seale.

This research project is carried out in cooperation with the *Hans Huber GmbH Maschinen- und Anlagenbau, Berching* and supported by the *Bayerisches Staatsministerium für Landesentwicklung und Umweltfragen* within the Bavarian research community BayFORREST.

REFERENCES

[1] Neeße, Th. and Schricker, B. (1997). Reinigung ölkontaminierter Sandfangrückstände mittels Mahlattrition. Berichtsheft 7 zum 5.Statusseminar BayFORREST an der TU München, 233-242.

The distribution of mineral oil pollutants on different particle size fractions

J. Dück, Th. Neeße, R. Breiter

Department of Environmental Process Engineering, University of Erlangen-Nuremberg, Schottkystraße 10, D-91058 Erlangen

Keywords: soil remediation, fine particles, mineral oil, adsorption, distribution coefficients

Physical soil remediation by soil washing is based on the dependency between particle size and contaminant distribution [1]. In general it is assumed, that there exists a linear relation between the adsorbed concentration K of contaminant and the specific particle surface area O_m according to the equation $K = b \cdot O_m$ with the constant b of adhesion. Practical experience has shown that this linear relationship is not held up in every case. Furthermore, contaminant exchange between the different particle size fractions can occur. In order to study these relationships, experiments with the following model materials were carried out:

Mixtures of three size fractions with the same mass percentage of glass balls (60 – 110 µm, 220 – 260 µm, 590 – 720 µm) and quartz sand (120 – 185 µm, 330 – 450 µm, 700 – 950 µm) were chosen. The mixtures of these three fractions were contaminated and then fractionated again by sieving.

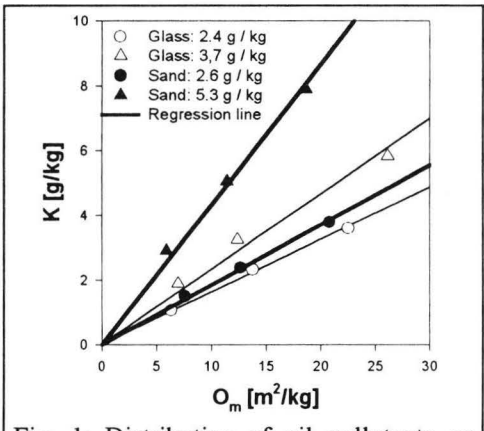


Fig. 1: Distribution of oil pollutants on dry-sieved glass and sand mixtures

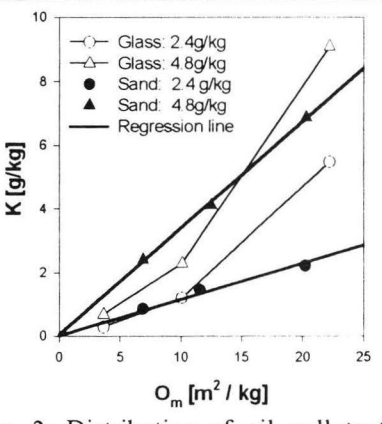


Fig. 2: Distribution of oil pollutants on wet-sieved glass and sand mixtures.

The measured contamination after fractionating by dry-sieving and wet-sieving is presented in Fig. 1 and Fig. 2.

In agreement with the expectation, there exists a linear relationship for quartz sand in both cases. In the case of wet-sieving glass balls the contaminant is transported by water

from the coarse fraction (upper sieve) to the fine particles collected on the lower sieve. These fine particles serve as collector for the mineral oil.

Fig. 3 shows the contaminant distribution of glass balls for two different preparation methods:

First method: The whole contamination of 2,4 g/kg was introduced into the mixture of the three fractions.

Second method: The same overall contamination was introduced only into one size fraction.

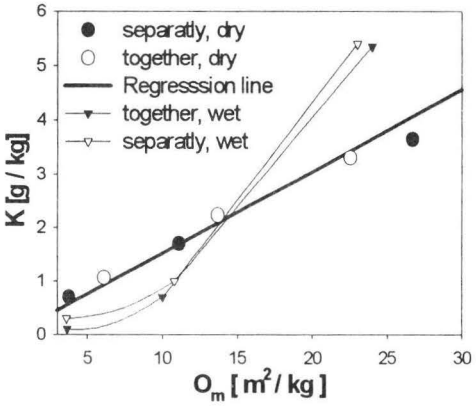


Fig. 3: Oil contaminant distribution on glass balls by different kinds of contamination and sieving

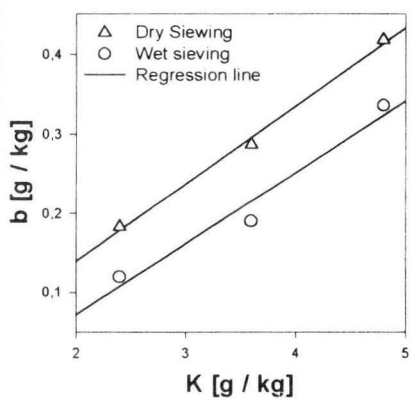


Fig. 4: Dependency of the adhesion constant b for dry and wet-sieved quartz-sand

As can be seen in Fig. 3 the contaminant distribution estimated after sieving was nearly the same in both cases, what can be interpreted with an intensive contaminant exchange. According to Fig. 4 the adhesion constant b for dry-sieving is higher in comparison with wet-sieving because of the emulsified contaminant rate in the water.

From the experiments it can be concluded, that more or less intensive contaminant migration takes place during wet processes of soil washing and substance investigations are not independent on the preparation methods. Microscopic observations show that adsorbed mineral oil doesn't cover the entire particle surface, but is concentrated in form of oil droplets (≈10 µm). The interparticle transport of the contamination is realized by oil droplet exchange during particle-particle-impact.

REFERENCES

[1] Neeße, Th. and Feil, A. (1993). The Decontamination Characteristic of Polluted Soils for Assessment of Suitability for Treatment of Former Industrial Sites. Aufbereitungs-Technik 1, 27 – 35.

OCCURRENCE AND FATE OF PLASTICIZERS (PHTHALATES) IN SOIL: LABORATORY AND FIELD STUDIES

Thomas Schiedek[1], Peter Grathwohl[2], Gerhard Einsele[2]

[1]Applied Geology Group, Darmstadt University of Technology, Schnittspahnstr. 9, 64287 Darmstadt, Germany, email: Schiedek@hrz2.hrz.tu-darmstadt.de
[2]Applied Geology Group, University of Tuebingen, Sigwartstr. 10, 72076 Tuebingen, Germany

Keywords: soil, screening, sorption, partitioning, distribution coefficients

S u m m a r y : The occurrence and fate of three phthalates in soil is investigated. A field screening in Southwest Germany showed that phthalates can be found in almost every soil sample, even in a depth of 80 cm below surface. The nonlinear Freundlich isotherms obtained from sorption experiments indicate a partitioning as well as an adsorption process. According to these results, the transport of the phthalates in soils is probably due to a non-equilibrium transport by preferential flow.

INTRODUCTION AND METHODS

The scope of this work was to investigate the occurrence and fate of three widely used phthalates (plasticizers), Dimethylphthalate (DMP), Di-n-butylphthalate (DBP) and Di-(2-ethylhexyl)-phthalate (DEHP), in soils in Southwest Germany (Fig. 1). For this field screening campaign a new method was developed for the extraction of phthalates from soils using a low toxic supercritical fluid (CO_2-SFE). This method allows a fast extraction of all three phthalates investigated. The background contamination, which is a serious problem during extraction and analysis of phthalates, is kept at a minimum. 63 soil samples were taken from 20 sampling locations with a small steel driller. As far as possible, samples were taken from 20 cm, 40 cm, 60 cm and 80 cm below surface and extracted by CO_2-SFE. The qualitative and quantitative analysis was performed with a GC-MS-system with a SCAN-run followed by a SIM-run using internal standards (Schiedek, 1995).

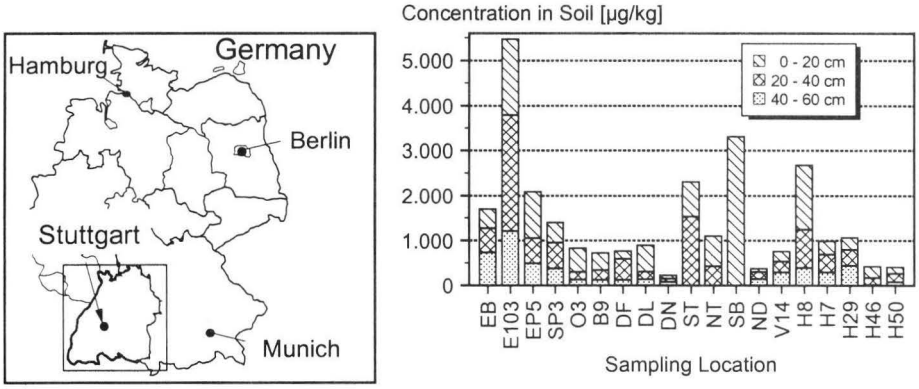


Figure 1: Occurrence and distribution of the phthalates investigated in soil (left: study area; right: sum of DMP, DBP and DEHP in µg/kg dry mass at different depths).

RESULTS

The results of the soil screening show that the phthalates investigated can be found in almost every sample. The phthalate distribution pattern in a sample often reflects the economical importance of each phthalate (DEHP>DBP>DMP). The spatial variability of the soil concentrations ranges over several orders of magnitude. Hence, the observed

concentrations range from a few µg/kg up to several mg/kg dry mass (Fig. 1). The vertical distribution, however, also shows an irregular distribution pattern. In some profiles even at a depth of 80 cm below surface phthalates can be found at higher concentrations than in the surface layer.

In order to investigate the sorption of phthalates onto soils, batch experiments under equilibrium conditions were performed with DBP as a chemical probe for phthalates. Samples were taken from a typical soil profile in Southwest Germany from different soil horizons from 0-100 cm below surface (RH-, Ah-, Bv-, Go- and Gor-horizon in Fig. 2). Analysis was performed with a HPLC-system according to an internal standard (Schiedek, 1995).

The nonlinear Freundlich isotherms indicate that sorption is due to a 'partitioning' as well as an adsorption mechanism (Fig. 2, left). The results of the batch experiments also show that the sorption of DBP onto soils depends on the content of organic matter. Hence, in a typical soil profile sorption (distribution coefficients) decreases with depth (Fig. 2, right). The organic carbon normalized sorption coefficient K_{oc} , however, is within the same order of magnitude throughout the profile. These results are considered to be valid for all phthalates, although for quantitative descriptions the adsorption mechanism have yet to be fully evaluated.

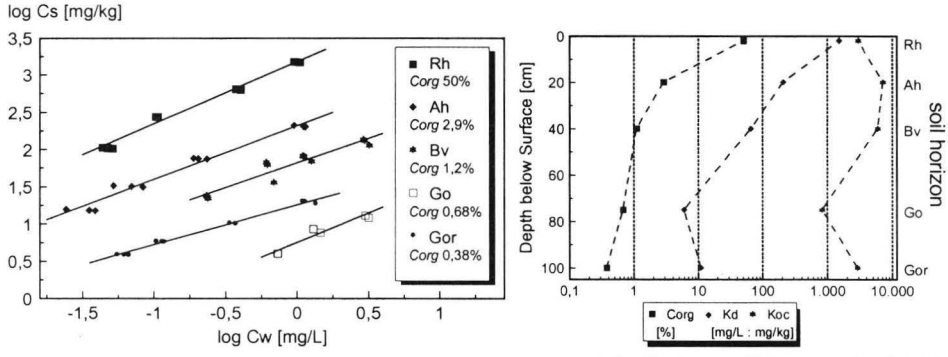


Figure 2: Sorption isotherms (left, solid line: Freundlich model) and distribution coefficients vs. depth (right) for DBP from soil batch experiments.

CONCLUSIONS

We conclude that the observed concentrations in soils of the phthalates investigated are due to a strongly varying atmospheric input (Schiedek, 1995). The vertical distribution pattern within a soil profile is probably due to a non-equilibrium transport by preferential flow, which also shows that phthalates can pass the soil (sorption) barrier. Hence, an impact on ground water quality is very likely.

REFERENCES

Jobling, S., Reynolds, T., White, R., Parker, M.G., Sumpter, J.P. (1995): A variety of environmentally persistent chemicals, including some phthalate plasticizers, are weakly estrogenic.- *Environ. Health Perspect* 103: 582-587.

MÜLLER, J., KÖRDEL, J. (1993): Occurrence and fate of phthalates in soil and plants.- In: Proceedings of the second European Conference on Ecotoxicology, Sloof, W., de Kruijf, H. (eds.): 431-437.

SCHIEDEK, T. (1995): Impact of Plasticizers (Phthalic Acid Esters) on Soil and Groundwater Quality.- In: Proceedings of the 'International Conference on Groundwater Quality: Remediation and Protection (GQ95)', Kovar, K.&Krasny, J. (eds.), IAHS, Prague 15.-18. May 1995.

IMPACT OF DIESEL POLLUTION ON SOIL MICROBIAL ACTIVITY AND NEMATODE COMMUNITIES

R A Jefferies[1,3], B. Boag[1], R. Neilson[1], D. Crabb[1], R.E. Wheatley[1], K. Ritz[1], H. Duncan[2].

[1] Scottish Crop Research Institute, Invergowrie, DUNDEE, DD2 5DA, UK
[2] Department of Chemistry, University of Glasgow, GLASGOW, G12 8QQ, UK
[3] Present address: Department of Plant Biology, SAC Auchincruive, AYR, KA6 5HW, UK

Key words: diesel oil, ecological effects, hydrocarbons, microbial activities, soil fauna

SUMMARY

The effect of diesel oil contamination on the structure and function of the flora and fauna in a mineral soil was examined in a glasshouse experiment. Results of the experiment demonstrate a modification of the native microbial population to one capable of effectively utilising diesel as a substrate. Growth of the adapted population led to an increase in microbial-feeding nematode species. The dramatic change in the size and composition of the nematode population suggests their potential use as bioindicators at oil polluted sites.

Soil inhabiting micro-organisms can be affected by petroleum contamination and certain bacteria and fungi are known to have the ability to degrade petroleum hydrocarbons. A glasshouse experiment was undertaken to investigate the impact of diesel pollution on the structure and function of the flora and fauna in a mineral soil The experiment, set up in lysimeters 20 l in volume, comprised 4 replicates of 5 levels of diesel (0, 12.5, 25.0, 37.5, and 50 g kg^{-1}) incorporated uniformly throughout the soil. Soil microbial activity was assessed at intervals by measuring substrate induced respiration (Ritz and Wheatley, 1989) using additions of glucose or diesel as supplementary substrates.

Six weeks after the incorporation of diesel, basal respiration rate increased in treatments receiving diesel (Table 1) indicating the utilisation of the diesel as a substrate by the soil microbial population. Inclusion of glucose in the substrate-induced respiration assay increased the rate of microbial respiration in all treatments, but inclusion of diesel in the assay had no effect on the rate of microbial respiration. This suggests that at this stage, although soil microbial populations were utilising the diesel in the treated soils, their activity was not limited by availability of diesel substrate, and that the community could utilise glucose more effectively than diesel.

At 24 weeks after incorporation of diesel, basal respiration rate in the control was similar to the rate measured at 6 weeks. In soils in which diesel had been incorporated, both basal respiration and rates in assays supplemented with glucose

were, in general, increased compared with rates measured at 6 weeks. Addition of a diesel supplement to the assay at this stage increased respiration rate compared with either the basal rate or the rate in assays with supplementary glucose. However, the magnitude of the increase in respiration diminished with increasing amount of diesel incorporated into the soil. This suggests that the microbial populations had adapted to ones well capable of utilising diesel as a substrate. The activity of populations was substrate limited in treatments with low to intermediate levels of diesel incorporated into the soil but not in the treatment with the highest level of diesel incorporation.

A week after the incorporation of the diesel the total nematode numbers had decreased in diesel amended soils by approximately 78% of that in the controls but these same nematode populations had risen to 204% and 507% of that of the controls after 4 and 15 months respectively. The increase after 4 and 15 months was solely due to 1 *Aphelenchus* sp. and 1 *Acrobeloides* sp. All other nematode species/genera were decreased to undetectable levels by the diesel amendments. The different concentrations of diesel had no significant differential effect on nematode numbers.

The experiment demonstrates a modification of the native microbial population to one capable of effectively utilising diesel as a substrate. Growth of the adapted population led to an increase microbial- feeding nematode species. The dramatic change in the size and composition of the nematode population suggests their potential use as bioindicators at sites polluted by petroleum products.

Table 1. Substrate induced respiration (mg CO_2-C/g soil/h) in soils 6 and 24 weeks after incorporation of diesel in to the soil.

Basal Respiration Rate

Week	Diesel incorporated into soil (g kg^{-1})				
	0	**12.5**	**25.0**	**37.5**	**50.0**
6	2.6	5.6	7.5	6.4	5.8
24	2.8	13.3	21.7	17.3	21.9

Respiration Rate with Glucose Supplement in the Assay

Week	Diesel incorporated into soil (g kg^{-1})				
	0	**12.5**	**25.0**	**37.5**	**50.0**
6	10.1	10.2	11.8	10.8	7.2
24	11.9	15.4	24.0	14.9	27.4

Respiration Rate with Diesel Supplement in the Assay

Week	Diesel incorporated into soil (g kg^{-1})				
	0	**12.5**	**25.0**	**37.5**	**50.0**
6	3.0	4.7	6.9	6.6	6.2
24	3.1	22.2	29.8	24.9	19.2

Statistical Significance

	Basal Respiration	**Respiration with Glucose Supplement**	**Respiration with Diesel Supplement**
Diesel	<0.001	0.01	<0.001
Week	<0.001	<0.001	<0.001
Diesel.Week	<0.01	NS	<0.001
SED (58 d.f.)	2.58	4.06	3.35

REFERENCES

Ritz, K. and Wheatley, R.E. (1989) Effects of water amendment on basal and substrate-induced respiration rates of mineral soil. *Biology and Fertility of Soils 8: 242-246.*

GROUNDWATER CONTAMINATION ON SMALL CONTAMINATED SITES - REMEDIATION BY SAMPLING ?

Ekkehard Petzold [1], Herbert Tramm [2], Dirk Veltrup [3]

[1] Dr. Petzold, Sachverständigenbüro / Dr. Petzold - Consult, Weißenburgstr. 14, D 48151 Münster, Germany
[2] Umweltbehörde Hamburg, Abt. Gewässer- und Bodenschutz / Environmental Authority, Dept. of Water- and Soil Protection), Billstr.84, D 20539 Hamburg
[3] FB Geowissenschaften, Universität Münster, Toppheideweg 44, D 48161 Münster, Germany

Key words: Groundwater remediation, sampling techniques, chlorinated hydrocarbons, polycyclic aromatic hydrocarbons (PAH), volatile organic compounds (VOC), pumping

SUMMARY
Groundwater sampling is usually done after pumping groundwater for a certain time to clear the well. On small contaminated sites resp. in small contamination plumes this can mean, that the plume might be pumped away before taking the groundwater samples. A layerwise sampling with packers and special samplers gives better results.

RÉSUMÉ
Dans les sites contaminés, il faut pomper une quantité minimale d´eau souterraine, avant de prendre un échantillon d´eau. Cette quantité est atteinte, si la conductibilité, la température et le pH sont constants. Dans les petits sites contaminés, en particulier dans le cas d´une petite extension de l´eau contaminée, il existe la possibilité d´ assainir la contamination par échantillonage. Pour cette raison, il est nécessaire d´utiliser un matériel spécifique pour prendre des échantillons stratifiés.

ZUSAMMENFASSUNG
Pumpproben aus kontaminierten Grundwasserleitern mit vorausgehendem Freipumpen bis zur Parameterkonstanz sind üblich. Bei kleinen kontaminierten Standorten bzw. Grundwasserschäden besteht dabei die Gefahr, den Schaden durch Probenahme zumindest vorübergehend zu "sanieren" und dabei verfälschte Ergebnisse zu erzielen. In solchen Fällen sind Schöpfproben und Packer sinnvolle Alternativen.

THE PROBLEM: GROUNDWATER SAMPLING TECHNIQUES

Groundwater investigation on contaminated sites or monitoring of groundwater remediation require sampling from groundwater wells. Usually a dipper is used when sampling at oil contaminations. In other cases samples are taken by pumps, after initial pumping - usually 3 times the content of the observation well resp. borehole. We made investigations to find out, if this standardized sampling will yield good results also on small contaminated sites. The results show, however, that this way of sampling is not applicable to small sites.

A SMALL GROUNDWATER CONTAMINATION: WHAT CAN GO WRONG

During soil investigations in the vicinity of a dry cleaning very high soil vapor contents of chlorinated hydrocarbons were detected. The ground consists of medium and fine sand with loamy lenses. Groundwater is at about 13 m below surface, and the aquifer

base at about 27 m. The size of the contaminated dry cleaning site was less than 2000 m^2. A groundwater observation well was placed downstream just aside the site, with a filter length from about 5 to 27 m below surface. Analyses of soil samples - one per meter - showed soil contaminations from 2 m up to 27 m below surface, showing a straight movement of the chlorinated hydrocarbons down to the aquifer base, passsing the unsaturated and saturated zones. Before taking groundwater samples the observation well was pumped clear for about 90 minutes, until pH and conductivity were constant. 2000 l water have been pumped out, and the groundwater level did not really change. The analyzed water sample was nearly free of contaminants.

PROBLEMS TO THINK ABOUT

The small contaminated site shows a limited horizontal, but a strong vertical extension of the contamination. Groundwater movement was slow, so there was no real contamination plume. Due to the small horizontal extension there was only a small amount of contaminated water, which has been pumped away before sampling. Constant pH and conductivity after 90 minutes confirm, that there was already fresh and uncontaminated water coming from the uncontaminated sides. Sampling from this clean water yields very low contamination values.

Additional uncertaincies to be checked during the investigations:
- The exact horizontal water flow during pumping is unclear due to many loamy parts (lenses) in the saturated zone;
- Installation of the pump and pumping will influence existing groundwater layers.
- Pumping and sampling evaporates the chlorinated hydrocarbons from the water in the well, and analyzed samples will show a lower contamination as real.

This means: Under these circumstances the evaluation of the contamination and the remediation planning are based on unreal data.

What happened to the chlorinated hydrocarbons in the groundwater? Due to their high density they sink down towards the aquifer base and follow the base inclination, which is not always the same direction as the groundwater flow.

CONCLUSIONS

For a better data base and exact decision making some aspects should be considered, especially if the groundwater contamination has only a small horizontal extension, and/or volatile organic compounds are involved:
- Initial pumping for a longer time seems to cause problems and unreal results.
- Initial pumping requires always a continous control of basic ("on-site"-)parameters, like pH and conductivity.
- Constant values can mean, that the contamination is already "remediated".
- Layerwise sampling (using a special dipper) without whirling the water in the well yields better results for better interpretation.
- Packers might be necessary depending on the depth of the well and the geology.
- The observation of layers and loamy parts (lenses) is important when constructing the observation well and must be considered when selecting filter parts. Otherwise contaminants will find bypasses from top downwards, and packers will not work.
- Placing observation wells has to consider the inclination of the aquifer base, especially with high density (>1) contaminants (chlorinated hydrocarbons, PAH).
- The latter requires, of course, filtered wells just into the aquifer base.

Last but not least: Sampling by pumping is still possible, but you must be sure not to "remediate" the contamination just by sampling.

HIDDEN CONTAMINATED SITES
SPECIAL TREATMENT AND FINANCIAL ASPECTS

Herbert Tramm[1], Ekkehard Petzold[2]

[1] Umweltbehörde Hamburg, Abt. Gewässer- und Bodenschutz / Environmental Authority, Dept. of Water and Soil Protection, Billstr. 84, D 20539 Hamburg, Germany

[2] Dr. Petzold, Sachverständigenbüro / Dr. Petzold - Consult, Weißenburgstr. 14, D 48151 Münster, Germany

Key words: Aromatic hydrocarbons (BTEX), halogenated hydrocarbons, volatile organic compounds (VOC), groundwater and soil contamination, hazardous goods, experts for environmental contaminations

SUMMARY
Unexpected soil or groundwater contaminations, e.g. appearing during excavations, require: 1. immediate rescue activities and risk management, 2. averting an expensive interruption of excavation / construction works, and 3. immediate evaluation of circumstances (cause and age of contamination), to avoid later-on discussions about responsibilities and payment obligations, due to unintended annihilation of evidences.

KURZFASSUNG
Die Entdeckung bisher unbekannter Altlasten, z.B. bei Aushubarbeiten, erfordert:
1. Sofortmaßnahmen zur Gefahrenabwehr, 2. die Abwendung eines kostenträchtigen Baustillstands (soweit machbar), und 3. sofortige Erkundungen zu Schadenursache und Schadenalter, um nachträglichen Streit um Kostenzuweisung und Verantwortlichkeiten wegen unachtsamer Vernichtung von Beweismitteln möglichst auszuschließen.

RÉSUMÉ
Découvrir des contaminations inconnues en sol ou en eaux souterraines, par exemple pendant des excavations, demande: 1. Mise en place de mesures immédiates pour se défendre contre les dangers, 2. Défense d´arrêts onéreux du chantier (si possible), 3. Recherches concernant la cause et l´age des contaminations, pour éviter des discussions successives sur les responsabilités, les obligations de paiement, ou l´anéantissement par mégarde des preuves.

THE PROBLEM: CONTAMINATED SITES

Groundwater and/or soil contaminations are often not detected at the moment or in the place they occur (e.g. leakage of an underground storage tank, broken underground pipeline). Many times these contaminations appear during excavations or in downstream wells.

When these hidden contaminated sites turn up, they need a treatment which has to be different from other, already known, contaminated sites.

Thus, 3 types of contaminated sites have to be distinguished:
1. Well-known sites, already registered in maps, documents, or evidently to be seen ("old factory", etc.)
2. Sites contaminated by accidents or averages with dangerous goods

3. Inconspicous sites, where unknown contaminations turn up accidentally, e.g. during construction works or excavations.

In the first case ("well-known contaminated site") there is no need for any emergency actions, e.g. to protect the groundwater, because the environmental damages exist already for a couple of years. There is sufficient time for organisation, investigation, evaluation and remediation planning. A time budget can be set up, and responsibilities and financiers are already defined. Alternative remediation techniques and competitive offers can be weighted, and excavations and construction works can be planned in a way, that there will be no temporary and expensive(!) stop in construction works due to unexpected underground contaminations.

The second case ("accident") gives no time for planning, but requires immediate correctice actions to protect human life, groundwater, surface water or other goods. These accidents, for instance an oil spill, are unpredictable, but on the other hand clear, because type and amount of the spilled dangerous goods are mostly known:
a) Industrial plants using dangerous goods know about their hazards, have emergency plans already set up and rescue services ready to go.
b) Transport accidents with dangerous goods on roads or railroads can be handled, because transport documents and vehicle lettering give sufficient information about type and amount of hazardous transport medium.

In the third case ("hidden contaminated site") the groundwater and/or soil contamination appears unexpectedly. Often the former land use of the site is unknown. The site was not "suspicious", what means: Type, amount, danger and extension of the contamination are (in opposition to the second case) unknown. This makes it difficult to decide immediately and efficiently about rescue activities or further investigations. Very important to do: Immediate investigations to collect evidences and to find out the source of contamination. This gives a better state to the authorities to reclaim the money they spent for rescue actions or other first aid, for instance from (probably involved) insurances or from former site owners.

The Environmental Authorities (Umweltbehörde) Hamburg have to handle about 100 "hidden" (unexpected) contaminated sites per year with the permanent risk of spending much money for emergency and remediation actions, which might never return.

CONCLUSION

The unexpected discovery of "hidden" underground contaminations needs appropriate experts, who are experienced both in handling "well-known contaminated sites" without any hurry, and also in accidents with hazardous goods. This expert has - in cooperation with the involved authorities - to worry about investigations to find the source of contamination and to collect evidences, because many of these cases end up with a litigation to find out who pays for the remediation.

Annotation: There are, among others, two types of official experts (*öffentlich bestellte und vereidigte Sachverständige*) in Germany: for "contaminated sites" (*Altlasten*) and for "hazardous goods" (*wassergefährdende Stoffe*). The above discussed cases do not require a new type of expert, but appreciation among the existing experts for these problems.

PREDICTION OF BIOAVAILABILITY OF PERSISTENT ORGANIC POLLUTANTS BY A NOVEL EXTRACTION TECHNIQUE

Brian J. Reid, Kirk T. Semple and Kevin C. Jones.*
Dept. Environmental Science, Lancaster University, Lancaster, LA1 4YQ, UK.
Tel: 01524 594534. Fax: 01524 593985. E-mail: k.semple@lancaster.ac.uk

Keywords: *Soil, Bioavailability, Extraction, PAHs.*

Introduction

It has been observed that as compound soil contact time increases, compound availability decreases (Hatzinger and Alexander, 1995). This phenomenon has been termed "ageing". As ageing proceeds, organic compounds can become sequestered into the soil matrix, resulting in their removal from the bioavailable fraction (Jones *et al*, 1996). For the successful application of a bioremediation strategy to contaminated land, it is essential that target pollutants are present in a bioavailable form. It is proposed that if ageing could be monitored by an extraction technique which emulates the soil biological vector then, prediction of the bioavailable fraction may be possible. In theory, a solution of cyclodextrin (Figure 1) could be used to extract pollutants from contaminated soil. Thus "available" non-polar organic molecules would transfer to the hydrophobic cyclodextrin cavity. It is hypothesised that owing to the greater size of the cyclodextrin macromolecule, in comparison to solvent molecules currently proposed to reflect bioavailability (Kelsey *et al*, 1997), a more accurate determination of the bioavailable fraction will be obtained. We report here a procedure for the extraction of aged compounds from soils using hydroxypropyl-β-cyclodextrin (HPCD) in a buffered aqueous solution.

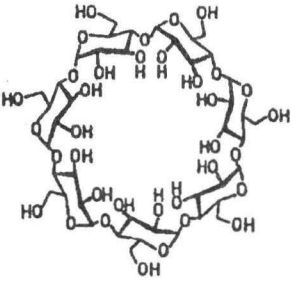


Figure 1: β-Cyclodextrin

Procedure

A sandy loam soil was collected from a rural hillside environment. The soil was air dried and then subsequently passed through a 2 mm gauge sieve to remove roots and vascular material. A single step spiking/rehydration procedure (Reid et al., 1998, submitted) was used to introduce 10 mg kg^{-1} ^{14}C-9-phenanthrene (51 Bq g^{-1}) to soil (250g). Incubations were produced in advance of their extraction date and allowed to age. In this way compound ageing times of 0, 41, 70 and 224 d were obtained. Total activity present in the soil samples was determined by sample oxidation (Canberra Packard 307 Oxidiser) of six 1g soil samples prior to cyclodextrin extraction.

Experiment 1: Solutions of HPCD were prepared in pH 8 buffer (K_2HPO_4 / KH_2PO_4) to provide a concentration range of 0 to 20 mM. These solutions were then pipetted (25 ml) in triplicate into Teflon centrifuge tubes containing approximately 1.2 g of freshly spiked soil. Blank extractions produced in duplicate were also prepared using unspiked soil The tubes were then shaken at 150 rev min^{-1} on a flat bed shaker for 20 h. After this time the tubes were centrifuged at 27000 *x g* for 20 min. The supernatants were

sampled (6 ml) in duplicate and added to Ultima Gold XR (Canberra Packard) liquid scintillation cocktail (14 ml). Analysis was accomplished by liquid scintillation counting (Canberra Packard Tri-Carb 2250CA analyser)

Experiment 2: A solution of HPCD was prepared in pH 8 buffer (K_2HPO_4 / KH_2PO_4) to provide a concentration of 25 mM. The aged soils were then extracted, sampled and analysed as described in Experiment 1.

Results and Discussion

Experiment 1: As the concentration of HPCD increased extraction efficiency was also increased (Figure 2). At a HPCD concentration of 20 mM the extraction was effectively 100% efficient (Figure 2), as might be expected of unaged compound. Given these findings a HPCD concentration of 25mM was employed in future extractions.

Experiment 2: The extraction of soils containing aged compound indicate a decrease in availability with increased compound soil contact time. Both the total extraction and the HPCD component only, indicated an initial rapid phase of compound sequestration, followed by a subsequent slower phase. The buffer component when considered independently indicated an increase in compound extractability as compound soil contact time increased. This may be related to the transfer of compound to buffer extractable organic matter with time.

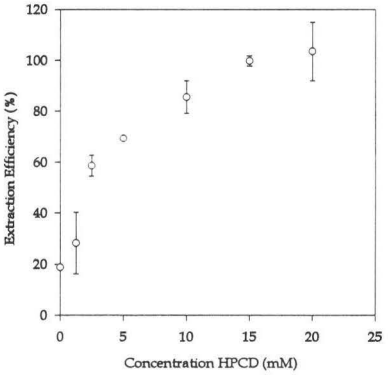


Figure 2:
Extraction of Freshly Spiked Soil using HPCD solutions of increasing concentration

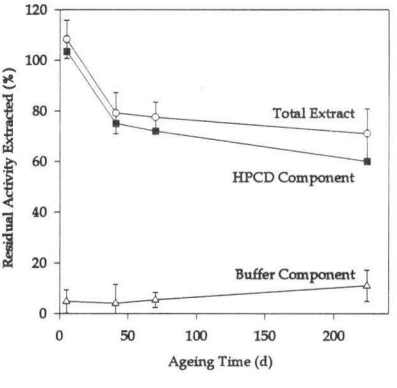


Figure 3:
Extraction of Aged compound from soils using HPCD solution at a concentration of 25mM

References

Hatzinger, P. B.; Alexander, M. **1995,** *Environ. Sci. Technol.* 29, 537-545.

Jones, K.C.; Alcock, R. E.; Johnson, D. L.; Northcott, G. L.; Semple K. T.; Woolgar, P. **1996,** *Land Contam. Reclam.* 4, 189-197.

Kelsey, J. W.; Kottler, B. D.; Alexander, M. **1997,** *Environ. Sci. Technol* 31, 214-217.

Reid, B. J.; Northcott, G. L.; Jones, K. C.; Semple, K. T. *Environ. Sci. Technol.* (Submitted)

THE USE OF ENVIRONMENTAL ISOTOPES AS LEACHATE INDICATORS IN SITE INVESTIGATION STUDIES

O. Kissling[1], W. Balderer[1] and P. Jordan[2]
[1] Engineering Geology, ETH-Hönggerberg, CH-8093 Zurich, Switzerland
[2] AWW des Kt. Solothurn, Rötihof, CH-4500 Solothurn, Switzerland

Key words: abandoned waste disposal sites, site investigation, isotope methods, microbial activity

In recent years a number of different investigation and analysis methods have been proposed in Switzerland, in an attempt to assess the influence of abandoned, legal or illegal waste disposal sites on the quality of ground and surface water. However, very little attention has been paid to the use of environmental isotopes for the investigation of contaminated land.

So far, isotopes have been used mainly to determine:
- the age and/or the residence time of the ground water (^{3}H, ^{14}C)
- the mean infiltration altitude ($\delta^{2}H/\delta^{18}O$)
- the source and/or origin of the contamination ($\delta^{15}N$, $\delta^{34}S$)

The impact of a waste disposal site on ground water quality may be evaluated by comparing pollution loads upstream and downstream of the potential pollution source. This is common knowledge generally applied to conventionally analyzed hydrochemical parameters (i.e. anions, cations, organic compounds). Investigations carried out on six former waste disposal sites throughout Switzerland show that this philosophy is applicable to several environmental isotopes, too, as the conservative nature of many environmental isotopes makes them reliable tracers for leachate migration.

Tritium was used successfully in several groundwater pollution studies. Being part of the water molecule, tritium proved to be a perfect tracer wherever tritium-bearing material was deposited in a landfill and, thus, entered the water cycle. The most likely source of tritium in Swiss landfills are luminous paints used in the watch industry. Leachates from the investigated sites show tritium concentrations of up to several thousand TU. A less dramatic but nevertheless unequivocal situation is represented in figure 1.

Stable isotopes, including $\delta^{2}H/\delta^{18}O$, $\delta^{34}S/\delta^{18}O$ in sulphate and $\delta^{13}C$ were also analyzed in ground water and leachate samples. Contaminated samples generally show more positive δ-values. One reason for this fractionation is the bacterial activity occurring under anaerobic conditions within the landfill. During biologically induced reduction of sulphate, for example, the bacteria *Desulfovibrio* and other sulphate reducing species preferentially consume the lighter sulfur (^{32}S) and oxygen (^{16}O) isotopes, causing an enrichment of the heavier isotopes in the remaining sulphate (figure 2).

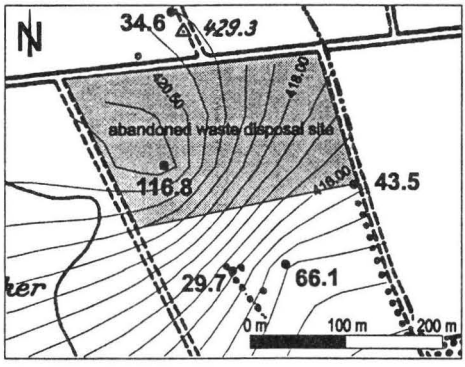


Fig.1 *Tritium concentrations in ground water at an abandoned waste disposal site*

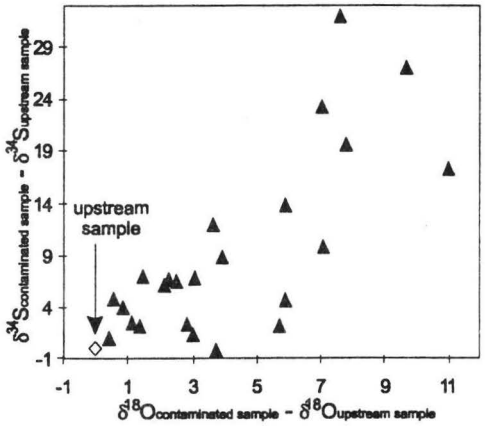


Fig. 2 *Relative changes in isotopic fractionation in the residual sulfate due to biological degradation (◆ upstream samples, ▲ contaminated samples; samples collected at 6 different waste disposal sites)*

The advantages of isotope techniques are:
- Low contamination potential during sampling and handling
- Although isotopic investigations may not directly be used for risk assessment studies, the isotopic signature of a downstream water sample can prove the landfill influence, even if other conventionally analyzed hydrochemical parameters don't show any significant increase in concentrations.

The use of environmental isotopes in contaminated site investigation studies can, in combination with hydrochemical data, help to determine the nature and the extent of potential contaminations caused by abandoned waste deposits.

References:

Clark, I. & Fritz, P. (1997) Environmental Isotopes in Hydrogeology, Lewis Publishers, Boca Raton, 328 p.

Hackley, K.C., Liu, C.L. & Coleman, D.D. (1996) *Environmental Isotope Characteristics of Landfill Leachates and Gases.* Ground Water, Vol.34, No.5, pp. 827 - 836

Nachtweyh, K., Rammensee, W., Hoefs, J. (1991) *Isotopengeochemische und geochemische Untersuchung der Kontamination von Deponiestandorten.* Müll und Abfall, pp. 421-435

AEROBIC DEGRADATION OF HEXACHLOROCYCLOHEXANES IN HIGHLY-CONTAMINATED SOILS FROM WASTE DUMPS OF THE CHLORINE-CHEMICAL INDUSTRY

V. Riis, W. Babel and D. Miethe

Centre for Environmental Research Leipzig-Halle Ltd., Permoserstrasse 15, 04318 Leipzig, Germany

Key words: contaminated soil, dumping site, hexachlorocyclohexane (HCH), pesticides, microbiological degradation, slurry, remediation

γ-hexachlorocyclohexane (lindane) was one of the most heavily-used insecticides in the 1960s and 70s. γ-HCH and other isomers are formed by chlorination of benzene under the influence of u.v. radiation. Only the γ-isomer, which amounts to 10-15% of the mixture, is active against insects. The bulk of the HCHs was deposited as waste on industrial dumps. Removal of this waste is only possible chemically by reversing the synthesis steps. However, there are also large amounts of soil on the dumps which have wide-ranging levels of contamination (from mg/kg up to a few g/kg), and for which microbial remediation may be possible. The aim of our investigation was to test the feasibility of this option.

Two highly contaminated soils from disposal sites of the chlorine-chemical industry at Bitterfeld (Saxony-Anhalt, Germany) were examined for the HCH-degrading potential of their autochthonous microorganisms. The soils were taken from 'Grube Antonie', which has 38.75 g HCH-mixture/kg waste and 'Fasanenkippe', which has 2.02 g HCHs/kg. An uncontaminated arable soil was also amended with HCHs, and included in the study.

In order to evaluate the microbial activity of the dump soils, the level of glucose-induced respiration, the capacity for the reduction of dimethylsulphoxide and hydrolysis fluorescein diacetate were determined. The densities of the microbial populations were also estimated by counting cells. The soils showed activities and cell numbers at the lower end of the range commonly found, corresponding to those of less fertile soils. High concentrations of HCH evidently have little inhibitory effect on the microbial activity, presumably because of the low water-solubility of the compounds (a few mg/l) which limits the availability and activity of the isomers.

The autochthonous communities of both dump soils degraded the present isomers α-, β-, γ- and δ-HCH. The mean elimination rates over 405 days amounted for the 'Antonie' soil to 15.1 mg α-HCH/kg·d and 3.22 mg γ-HCH/kg·d and for the soil 'Fasanenkippe' to 2.72 mg α-HCH/kg·d and 0.23 mg γ-HCH/kg·d. The latter value is so low owing to insufficient bioavailability. β-HCH is only degraded very slowly. For the soil 'Fasanenkippe' for instance, an elimination rate (microbial degradation + abiotic effects) of 0.22 mg/kg·d resulted. Assuming linear decrease, eight years would be necessary for complete decontamination. The complete degradation of β-HCH in the soil 'Antonie' (practically a soil/HCH mixture) would probably require 80 years.

δ-HCH is also degraded very slowly. As its level in the soil was low, this isomer is not critical for the success of remediation. A gradual degradation of α-, γ- and δ-HCH was

Contaminated Soil '98, Thomas Telford, London, 1998, 893–894

also found for the arable soil. The decrease of the HCH concentrations in the 'Fasanenkippe' soil is given in Figure 1.

Degradation proceeds more slowly in soils because of their inhomogeneity and the immobility of microorganisms. The distribution of the HCHs in the present soils is very heterogeneous (partly they occur as visible particles), which makes availability limited despite the high concentration. We therefore carried out experiments in shaking bottles with soil slurries and an isolated mixed culture. Even in suspension culture the degradation rate for β-HCH was below 1 mg/l·d. Degradation rates of up to 90 and 40 mg/l·d were found for α- and γ-HCH respectively. Attempts poisoned with $HgCl_2$ were used to determine abiotic elimination. Over a period of 7 weeks this amounted to about 1/4 of the original quantity.

In order to optimally use the degradation potential of the autochthonous microorganisms in the dump soils, we recommend the slurry technique. The physiological conditions must of course be optimised, first of all the chloric acid released must be neutralized. In this way it is possible to degrade up to 350 mg α- and/or γ-HCH per litre slurry over a period of 7 days. However, the level of β-HCH is decisive for the feasibility of remediation. Using a 1:5 slurry (soil to water mass), a soil with 70 ppm β-HCH can be decontaminated within two weeks. Difficulties result with higher concentrations:

1. The slurry technique requires reactors or reaction basins. Treatment over several weeks is not possible.
2. Using higher water/soil ratios does not provide a solution as the volume to be treated increase proportionally.

On the basis of our investigations, the remediation of heterogenous soils highly-contaminated with HCHs (but not more than 100 ppm β-HCH) by microbial degradation is possible if a suitable community is present, the slurry technique is used, and longer residence times are acceptable. HCH-degrading communities were present in both dump soils examined.

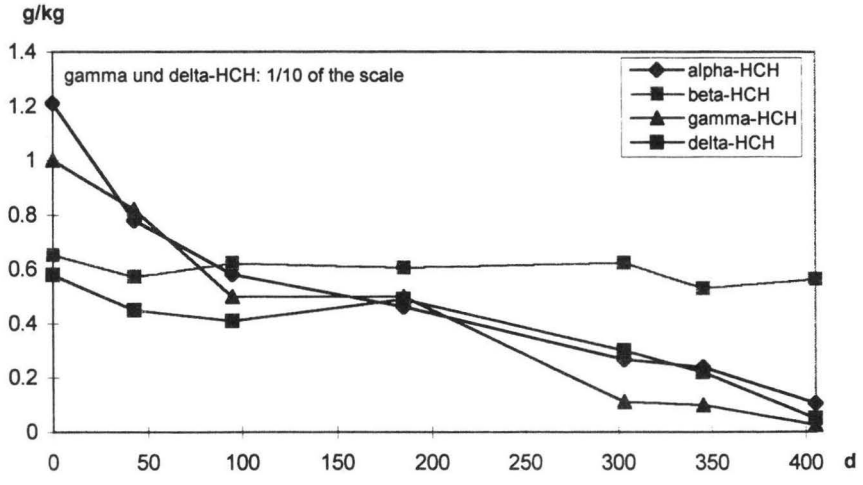


Figure 1. Decrease of HCH concentrations in the 'Fasanenkippe' soil

DEVELOPMENT OF A VALIDATION PROTOCOL FOR METHODS OF ANALYSIS OF CONTAMINATED SOIL

M. Kibblewhite[1], L. Heasman[2] and V. Forster[3]

[1]Hyder, Laboratories and Sciences, Science Park, Bridgend, Wales, UK
[2]M J Carter Associates, Station House, Atherstone, Warwickshire, England, UK
[3]Environment Agency, Steel House, Tothill Street, London, England, UK

Key words: analytical methods, monitoring procedures, QA / QC program, quality assurance, quality control.

SUMMARY

A draft validation protocol has been prepared which provides guidance on criteria which can be used to assess whether analytical method performance is satisfactory and on the approach laboratories can take to provide data which can be assessed against these criteria. The validation protocol provides a means by which the performance of specified analytical methods can be validated for different soil types.

When the method being validated relies on extraction of soil samples, followed by analysis of the extracts obtained, the instrumental or other analytical method which is to be applied to soil extracts should first be validated by estimating its method standard deviation. Initially, a five point traceable calibration including a zero level solution should be performed in duplicate on at least two separate days. The linear regression coefficient, calculated from the data resulting from analysis of the calibration solutions, should be significant at the 95% level of confidence. Then, to determine the method standard deviation of the instrumental determination, the lowest and highest calibration standards should be analysed in duplicate on eleven separate days. The results from this should be subjected to an analysis of variance and the error term from that used to calculate the method standard deviation. Ideally, this standard deviation needs to be less than 5% of the concentration expected in extracts of soils containing contaminants at the levels of interest. The standard deviation of the mean of measurements on the lowest calibration standard, multiplied by a factor of no less than three, should be used to estimate the limit of quantification for the analytical determination when it is applied to soil extracts and no data for test soils should be reported for which measured extract concentrations are less than this limit. As calibration standards do not contain interfering materials which may be present in soil extracts, the limit of quantification derived from their analysis may be incorrect; therefore if a representative soil extract is available which contains a concentration of analyte which is no greater than that in the lowest calibration standard, it is preferable that the standard deviation of the mean of measurements on this extract should be used to estimate the limit of quantification.

When the method being validated does not include an extraction step, the requirement remains to: firstly, establish a traceable five point calibration for which

the linear regression coefficient is significant at the 95% level of confidence and, secondly, to estimate the limit of quantification from the standard deviation of the mean of measurements on a sample containing the analyte at a concentration which is no greater than one tenth of that in the lowest calibration standard.

Following characterisation of the performance of the instrumental or other analytical determination, the complete method of soil analysis including any extraction steps has to be validated. If certified reference material soils are available with contaminant values obtained by application of the same method which is being validated, then the acceptability of the laboratories method bias should be tested by analysing these soils in duplicate on at least eleven separate days and then demonstrating, by means of *t* tests, that the results are equivalent to the expected values at the 95% level of confidence. Additionally, these results should then be subjected to an analysis of variance and the method standard deviation calculated from the error term. The overall means and standard deviations should then be compared with the published values for the reference materials. Ideally, the method standard deviation obtained should be less than 10% of the concentrations expected in a soil containing contaminants at the levels of interest.

When suitable certified reference materials are not available, test soils should be chosen for the validation which are broadly similar to those to which the method is to be routinely applied. This choice should take account of the types of natural soil "phases" present in the samples to be tested after validation, as well as the nature and expected concentration of past industrial or other contamination. Samples which are used for method validation must be sufficiently homogeneous to ensure that sub sampling errors are negligible compared to those arising from the analytical method. Each soil used for the estimation of method standard deviation should be analysed in duplicate on at least eleven separate days and the results for all soils subjected to an analysis of variance.

As a part of their initial and ongoing method validation, laboratories should participate in proficiency testing schemes to demonstrate that their experimental bias for soil analysis is within acceptable confidence limits.

A quality control regime should be continually used to ensure that the measured level of analytical performance is maintained. This can be done by, for example, analysing with each batch of test samples, the same samples which were used for method validation, or other well characterised samples such as reference materials, and plotting the results on statistical process control charts.

Preparation of the draft validation protocol was commissioned by the UK Department of the Environment, Transport and the Regions and the Environment Agency and has been assisted by advice and contributions from a working group on soil analysis.

LEACHING OF INORGANIC CONSTITUENTS FROM CONTAMINATED SOIL

Knut Ødegård[1)], Kåre Helge Karstensen[1)] and Walter Lund[2)]
[1)] SINTEF, P.O.Box 124, N-0314 Oslo, Norway.
[2)] Department of Chemistry, University of Oslo, P.O.Box 1033, N-0315 Oslo, Norway.

Keywords: chemical speciation, contaminated soil, heavy metals, ion exchange resins, leaching.

The degree of attenuation of a pollutant by soil depends to a large degree upon the water content of the soil. Above the water table there is an unsaturated zone of soil in which attenuation is more highly favoured. Normally soil has a greater surface area at liquid-solid interface in this zone so that absorption and ion-exchange processes are favoured. Aerobic degradation is possible in the unsaturated zone, enabling more rapid and complete degradation of biodegradable substances.

Heavy metals are particularly damaging to groundwater and their movement through the soil is of considerable concern. Heavy-metal ions may be sorbed by the soil, held by ion-exchange processes, interact with organic matter in soil, undergo oxidation-reduction processes leading to mobilisation or immobilisation, or even be volatilised as organometallic compounds formed by methylating bacteria. A large number of factors affect heavy-metal mobility and attenuation in soil. These include pH, pE, temperature, cation exchange capacity, nature of soil mineral matter, and kinds of soil organic matter present (Manahan 1994).

The application of leaching procedures to polluted or naturally contaminated soils is mainly focused to ascertain the potential availability and mobility of pollutants, its migration, to assess pollution levels in contaminated areas and in survey programmes. Leaching tests are used for predicting deficiency of essential elements, for potential toxicity assessment and to ascertain the probability for disease generation and in studies about the physico-chemical behaviour of elements in soils.

The speciation of the inorganic constituents in the leachates from leaching studies has been studied by the use of different analytical approaches.

References

Manahan, S.E. (1994), *Environmental Chemistry*. Boca Raton: Lewis.

The use of microbiological indicators for the determination of the quality of soils : application to a covered hydrocarbon polluted site.

B. Brohon & C. Delolme
Laboratoire des Sciences de l'Environnement, Ecole Nationale des travaux Publics de l'Etat, Rue M. Audin 69518 Vaulx-en-Velin Cedex, FRANCE

Key words : microbial activities, contaminated soil, hydrocarbons, heavy metals, soil properties

The chemical characterisation of pollutants in a soil does not give information on the environmental impacts on the ecosystem. The measurement of metabolic activity perturbations of the soil microflora can help to precise the toxic effects of the xenobiotics in a soil. The microorganisms activity level mainly depends on the agronomic characteristics of the soil. So, a comparison between the microbial activities and the soil's characteristics measured on different samples on a same soil can indicate the most disturbed zones. The aim of this work is to test the use of microbial activity measurement to determine the quality of a site polluted by hydrocarbons and covered.

Materials and Methods

The site chosen had received hydrocarbons during several years and then a part had been covered. Previous investigations (historical and physico-chemical) on this site allowed us to distinguish five different zones with different pollution characteristics. (Table 1)

Table 1 : Characteristics of each zone

Zone N°1	Zone N°2	Zone N°3	Zone N°4	Zone N°5
Reference area	Broken oil tank buried in soil	Traces of oil in depth	Oil spots on the surface	Oil spot on the surface and slicks in depth

A random surface sampling (3 to 11 samples) was made in each zone. The samples of each zone were mixed in order to have one representative sample for each. $pH_{(water)}$, pH_{KCl}, total N, organic C, volatile matter, conductivity, water content, total heavy metals, total hydrocarbons were measured on each zone [**2**]. INT-reductase, Phosphatase, Urease, Fluorescein diacetate hydrolysis (FDA), and Respiration were the chosen microbial activities [**1**]. A principal component analysis (PCA) is made on the data.

Results and discussion (fig.1)

The zone n°1 shows the highest activities except for FDA and is confirmed as the reference. The zones N°2, 3 and 4 have nearly the same microbial responses but the zone N°2 reveals very low urease and dehydrogenase activities. As a whole, the lowest microbial responses are measured on the zone N°5.

The PCA of agronomic data (fig.1) help to discriminate three groups of soils. The zone N°1 is the original soil, the zone N°2 contains the highest organic matter level and the zone N°3,4 and 5 have almost the same soil's characteristics except the conductivity. Considering both PCA, the zones 2 and 3 that reveal a close microbial behaviour have completely different agronomic characteristics, whereas zones 4 and 5 that have the same agronomic composition show different microbial activity levels. These differences can not only be explained by the concentration of pollutants. The hydrocarbons concentrations are not very high (<70 mg/kg of dry soil) and do not seem to be the determinant factor.

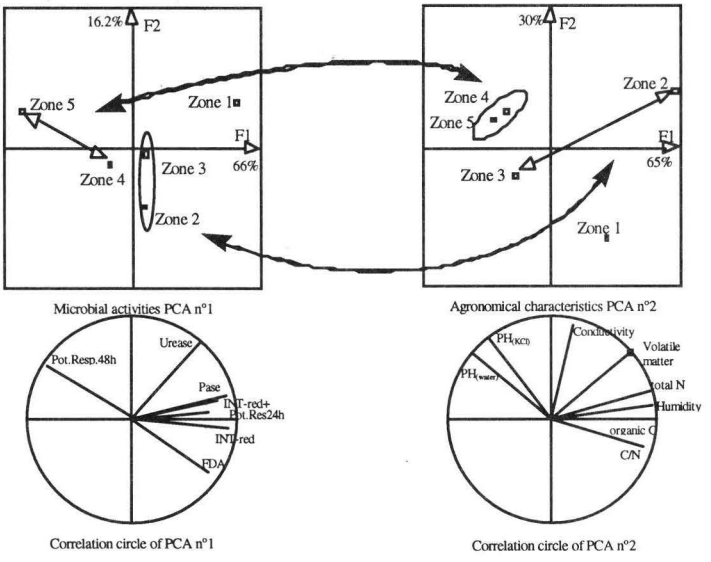


Figure 1 : PCA of physico-chemical and microbiological characteristics of the samples

Nevertheless, the heavy metals concentrations (in mg/kg dry soil) of the zone N°2 and N°5 (Ni : 842 N; Pb : 355; Cu : 98; Cr : 40 and Ni : 35; Pb : 146; Cu : 170; Cr : 39 respectively) are very high. It can explain the unexpected microbial activities responses between the zones 2 and 3 and between the zones 4 and 5. But the zone N°5 is not the most polluted zone and shows the lowest microbial activities. Many authors say that the level of microbial activity inhibition in polluted soils depends on the type of pollutant, its chemical form, its concentration, and the physico-chemical properties of the receiving environment [**5**]. Accordingly, the chemical analyses are not effective to reveal the pollutant impact on soil ecosystem. That's why it is interesting to combine different microbial activities [**4**] and to consider the polluted soil's characteristics in order to understand the xenobiotic responsibility in microbial perturbations measurements.

Conclusion

The study of the microflora of a covered hydrocarbon polluted soil seems to be interesting in the quality evaluation phase. The enzyme activity decrease reveals a dysfunction in the biogeochemistry of the soil [**3**]. This method could simplify the analytical part of the diagnosis phase of a site and help to determine the most polluted zones and the treatment to choose.

1-ALEF, K. & NANNIPIERI, P. (1995) *Methods in applied soil microbiology and biochemistry*. Academic Press, New York, 576 pages.

2-AUBERT, G. (1970) *Méthodes d'analyses des sols*. CRDP Marseille, 200 pages.

3-KANDELER, E., KAMPICHLER, C. & HORAK, O. (1996) Influence of heavy metals on the functional diversity of soil microbial communities. *Biology and Fertility of Soils* 23, 299-306.

4-NANNIPIERI, P., GRECO, S. & CECCANTI, B. (1990) Ecological significance of the biological activity in soil. In : BOLLAG JM. & STOTZKY, G. (eds) *Soil Biochemistry 6*, pp. 293-355.

5-TABATABAI, M. A. & FU, M. (1992) Extraction of enzyme from soils. In : BOLLAG JM. & STOTZKY, G. (eds) *Soil Biochemistry* 7, pp. 197-227.

QUALITY ASSURANCE IN THE ANALYSIS OF SOILS FROM LAND CONTAMINATION

V Forster[1], L Heasman[2] and M Kibblewhite[3]

[1]Environment Agency, Steel House, Tothill Street, London, SW1H 9NF, UK.
[1]Formerly at Laboratory of the Government Chemist, Queens Road, Teddington, Middlesex, TW11 0LY, UK.
[2]M J Carter Associates, Station House, Long Street, Atherstone, Warwickshire, CV9 1BH, UK.
[3] Hyder Environmental Laboratories, Mid Glamorgan Science Park, 2 Technology Drive, Bridgend, CF31 3NA, UK.

Key words: analytical methods, characterisation, contaminated soil, environmental investigations, quality assurance, quality of the soil.

Concern has been expressed for some time about the validity of analytical determinations made in connection with investigations for land contamination. The lack of confidence in analytical measurements made by laboratories in this field perpetuates perceived risks presented by land contamination. There is a need therefore to increase the confidence in analytical data by an improvement in quality at all levels in the analytical process from sampling to reporting. This paper summarises the recommendations presented in a UK Department of the Environment, Transport and the Regions/Environment Agency report[1] for best practice in quality assurance of the analysis of soil from land contamination.

Sampling Strategy. The sampling strategy should have a sound statistical basis. It should enable areas of significant contamination to be detected. Sampling guidance should be universally employed. An appropriately experienced and qualified chemist or other specialist should be on site during sampling.

Sampling Method. Sampling plans should be devised based on preliminary site investigations and should take into account the intended site use and other management issues. Sampling equipment and methods should be selected based on site specific sampling needs and should be cleaned prior to, between and after taking samples. The amount of sample needed should be assessed with care.

Sample Labelling. Samples should be labelled at the time of sampling with sufficient information to identify and locate the samples taken. A detailed sampling log should be completed at the time of sampling. Chain of Custody procedures should be employed to ensure traceability of samples from sampling to analysis to reporting of results. Sealing of samples may be necessary in some cases to detect unauthorised tampering.

Sample Transportation and Storage. Appropriate sample containers and sample storage must be employed to ensure that no contamination, loss of components or sample deterioration occurs. Samples should be transported to the laboratory and analysed as soon as possible after sampling. The time between sampling, delivery to the laboratory and analysis should be appropriate to the parameters being determined.

Initial Sample Treatment. Sample pre-treatment should follow standard guidance, maintain sample integrity and be accurately documented. Oversize material should be weighed and retained. Samples must be homogeneous prior to analysis.

Sample Digestion and Extraction. Laboratories should follow standard extraction procedures with validated performance criteria. The effectiveness and repeatability of the procedures should be demonstrated.

Instrumental Analysis. Methods selected should have been fully validated for the appropriate matrix and the laboratory performance criteria should be established and quoted. Instruments should be calibrated with standard solutions traceable to pure reference materials. Maintenance records for all analytical instrumentation should be retained. Appropriate matrix reference materials should be analysed where available to check for chemical interferences. Control charts should be prepared and maintained using standard solutions. Results should be rejected if they fall outside the calibrated range of the instrument used.

Treatment of results, statistical checks and the laboratory/client relationship. All report calculations should be independently checked by a senior analyst. Standard statistical procedures should be used to check data reliability. Report formats should be agreed with the client and an effective dialogue maintained. Confidence limits of the data should be provided to the client.

Quality Standards. All laboratories should seek independent approval of their quality system by accreditation to a recognised quality standard.

Method Validation. Laboratories should ensure that all methods are validated prior to use to ensure that stated performance criteria can be achieved. The degree of validation will depend on the performance data already available on the method.

Reference Materials. Reference materials should be used for method validation. Where materials are not available in-house matrix reference materials can be prepared for a typical range of soil types and analytes and independently checked.

Internal Quality Control. Control charts should be plotted for all analytical methods using standard statistical procedures. Documented procedures should be in place to deal with results that are outside the pre-set confidence limits.

Quality Control Samples. Quality control samples should be analysed including field blanks, trip blanks, analytical blanks, reagent blanks, blind samples, QC samples, spiked samples and duplicates.

Proficiency Testing Schemes. Laboratories should participate in soil proficiency testing schemes which have been developed in accordance with the International Harmonised Protocol[2].

[1] *Quality Assurance Associated with the Analysis of Soil from Land Contamination. UK Department of the Environment, Transport and the Regions/Environment Agency. In preparation.*

[2] *International Harmonised Protocol for the Proficiency Testing of Chemical Analytical Laboratories. Thompson, M. and Wood, R. Pure Appl. Chem., 1993, 65, 2123-2144.*

INFLUENCE OF SOIL CHARACTERISTICS ON ELIMINATION OF PENTACHLOROPHENOL

G. Barančíková[1], Z. Gergeľová[2]

[1] Soil Fertility Research Institute, Reimannova 1, 080 01 Prešov, Slovakia
[2]Soil Fertility Research Institute, Gagarinova 10, 827 13 Bratislava, Slovakia

Key words: Chlorinated hydrocarbons, degradation, soil, organic matter, clay

Pentachlorophenol (PCP) was used as a fungicide, herbicide, defoliant, insecticide and wood preservative for more than 60 years. Because of its toxicity and apparent ubiquity in the environment, PCP is the most thoroughly studied of chlorophenols. It has been reported as a contaminant of soils, sediments and natural waters as well as in food and human urine. In soil PCP may undergo biotic and abiotic degradation. The rate and extend of these processes depend on many microbial and environmental factors, among them soil properties play very important role.

The objective of this study was to investigate the effect of soil types with different basic soil physicochemical properties (clay content, quantity and quality of soil organic matter and pH) on the range and on the rate of degradation of PCP.

Five different soil types (Fluvi-eutric Gleyosol, Dystric Planosol, Calcaro-haplic Chernozem, Dystric Cambisol and Calcaric Regosol) were artificially contaminated with PCP at the level of 0.5 mg/kg in laboratory experiments. The selected soils represent the prominent soil types in Slovakia. The soil samples moisten to the level of 40 % of full water capacity were incubated at 21^{0}C in laboratory conditions. Content of pentachlorophenol in soil was determined by GC analysis of soil extract after 20, 45, 80 and 160 days of incubation. The range of PCP elimination was defined on the basis of the extent of this disappearance from soils.

The first results showed, that the extent and degradation rate of PCP varied according to the type of soil. After 20 days of incubation more than 50 % of PCP was eliminated from Fluvi-eutric Gleyosol and Dystric Planosol. However disappearance of pentachlorophenol from Calcaric Regosol and Calcro-haplic Chernozem was only 28 %, 32 % respectively.
Similar situation was observed also after 45 days of incubation.
Nevertheless, with time degradation rate of PCP was quite changed. After 80 days of incubation almost 95 % of PCP disappearance was found in Dystric Cambisol and Dystric Planosol . Approximately 90 % of PCP eliminated from Calcaric Regosol and Fluvi-eutric Cambisol. The lowest extent of PCP elimination was observed in Calcaro-haplic Chernozem (77 %).

Contaminated Soil '98, Thomas Telford, London, 1998, 903–904

In addition after end of incubation (160 days) the lowest extent of degradation was noticed in Calcaro-haplic Chernozem (94,5 %) and the highest PCP elimination was detected in Dystric Cambisol (98 %).
The single linear correlations between soil properties (clay content, organic matter, pH) and extent of PCP degradation was not detected (Table 1). However on the basis receiving results it can be seen that highest disappearance of pentachlorophenol was found in soil sample with the highest amount of organic matter.
Because not only quantity but also quality of soil organic matter can influence the fate of PCP in soil, relationship between humification degree of soil organic matter, characterized by some parameters of chemical structure of humic acids (carboxylic groups, degree of aromaticity and optical parameters) and the extent of elimination PCP was investigated. Significant negative linear correlations between parameters of humic acids and degradation of pentachlorophenol were confirmed (Table 1). Therefore it can be deduced that higher-humified organic matter with high degree of aromaticity and high content of carboxylic groups are expected to participate in the possibly tightly bound to PCP. In corresponding cases the chlorophenols may be less available to the microbes.

In conclusion it can be said, that degradation of PCP in different soil types is quite distinct. As regard of soil properties, it seems, quality of soil organic matter can considerably influence the fate of PCP in soil.

Table 1. Linear correlations between % of PCP elimination after 160 days of incubation (a) and soil/humic acids parameters

Y	X	R
a	pH	-071
a	Corg	0,65
a	clay	-0,39
a	COOH	-0,86**
a	α	-0,97**
a	$E^{1\%}_{6}$	-0,85*

COOH - carboxylic groups
α - degree of aromaticity
$E^{1\%}_{6}$ - the absorbance coefficient for 1 % HA solution at 600 nm

A NEW APPROACH FOR BIOMONITORING: ASSESSING DEGRADATION POTENTIALS FOR POLYAROMATIC HYDROCARBONS USING GENE PROBES

S. Meyer [1], R. Moser [2], A. Neef [1], U. Stahl [2], P. Kämpfer [1]

[1] Institute of Applied Microbiology, University Giessen, Senckenbergstraße 3, 35390 Giessen, Germany
[2] Institute of Biotechnology, Department of Microbiology und Genetics, Technical University Berlin, Gustav-Meyer-Allee 25, 13355 Berlin, Germany

Key words: aromatic hydrocarbon contamination, microbiological degradation, PAH (polycyclic aromatic hydrocarbon), biomonitoring, soil, waste waters

SUMMARY

Bacterial strains with the ability to degrade polyaromatic hydrocarbons (PAH) like phenanthrene and naphthalene were isolated from different soil samples and from wastewater. The strains were identified down to genus or species level by different identification methods like rRNA typing, fatty acid methylester analysis and biochemical tests in microtiterplates.
This pool of PAH degrading strains were examined for the presence of specific genes coding for dioxygenases involved in PAH degradation by polymerase chain reaction (PCR). Dioxygenase genes from isolates were sequenced and aligned with existing sequences for the development of oligonucleotide probes. These probes should be used for the detection of the potential for PAH degradation without time-consuming cultivation methods.

PAHs are widespread environmental contaminants containing two or more fused benzene rings. They are formed during the incomplete combustion of a variety of materials such as fossil fuels and organic compounds. Because of their genotoxicity there is a growing interest for the development of technologies to detoxify PAH-contaminated wastes. PAHs can be biologically degraded by certain bacteria, belonging to different taxonomic groups.
Eighteen bacterial strains with the ability to degrade phenanthrene and/or naphthalene were isolated from two wastewater treatment plants, from leakage water of a waste disposal site, from soil samples from a parking place and from tar oil contaminated soils. Using different identification methods, like typing with ribosomal ribonucleic acid-targeted probes, analysis of the fatty acid patterns of whole cell hydrolysates and miniaturized biochemical tests, the strains were identified as *Pseudomonas fluorescens, P. putida, P. mendocina, Comamonas testosteroni, C. terrigena, Acidovorax* spp., *Sphingomonas* spp., *Rhodococcus rhodochrous,* and *R. erythropolis.*
The degradation of phenanthrene or naphthalene by different isolates, examined by gaschromatographic determination of the remaining PAHs in the medium, led to similar results. The content of PAH decreased approximately proportional with the time. The optical density increased during this time period continuously. Generally, naphthalene degradation proceeds faster compared to the metabolization of phenanthrene.

Contaminated Soil '98, Thomas Telford, London, 1998, 905–906

The isolates were examined for the presence of an initial PAH dioxygenase and catechol 2,3-dioxygenase by a PCR based approach. These dioxygenases catalyze keysteps in the breakdown of PAHs.
Primers for amplification of fragments of the corresponding genes were selected from alignments of existing sequences. Regarding the initial dioxygenase only four sequences of different *Pseudomonas* strains exist, whereas 20 sequences of catechol 2,3-dioxygenases are deposited in data bases.
Initial dioxygenase: It was possible to amplify DNA fragments of the predicted size with the initial dioxygenase primers from strains belonging to the genus *Pseudomonas* which are able to degrade naphthalene and/or phenanthrene. No fragments could be amplified from any other strains. The initial dioxygenases of these strains seemed to be quite different from the *Pseudomonas* initial dioxygenases. The result of PCR was confirmed by hybridization experiments. Only digested DNA of the *Pseudomonas* strains hybridized with a gene probe against the initial dioxygenase.
Catechol 2,3-dioxygenase: Using a published pair of primers for PCR (Wikström et al., 1996) DNA fragments coding for catechol 2,3-dioxygenase could be amplified for all isolates belonging to the genus *Pseudomonas* or *Sphingomonas*. Specific amplicons for *Pseudomonas* isolates, possessing a catechol 2,3-dioxygenase could be received using another pair of primers. The negative results of the other strains could be either due to low homology of the genes or a complete lack of catechol 2,3-dioxygenase. For the two isolates *Comamonas testosteroni* the activity of this enzyme could be shown by photometrical measurement of the increase of the yellow-coloured ring fission product 2-hydroxymuconic semialdehyd. However it was not possible to amplify specific DNA fragments of these strains, even when more relaxed PCR conditions were chosen. This result could be explained by the low homology of the gene of the *Comamonas*-strains compared to the *Pseudomonas* and *Sphingomonas* genes.
The partial sequencing of PCR amplicons of different *Pseudomonas* isolates show that the sequences are more than 75 % similar to each other and to existing sequences of a so called "*Pseudomonas*"-group, for example *P. putida* P35 x. The sequences of *Sphingomonas* isolates are more than 75 % similar to the catechol 2,3-dioxygenase sequence of *S. yanoikuyae* B1 and form togehter a second "*Sphingomonas*"-group.
The obtained sequence information and published sequences were used for the development of oligonucleotides for the detection of catechol 2,3-dioygenase of these two groups. These oligonucleotides were applied in hybridization experiments of separated and blotted PCR fragments and DNA-dot-blots. One gene probe hybridized specifically with the PCR fragments of *Pseudomonas* isolates, whereas another showed only hybridization signals with PCR fragments of *Sphingomonas* isolates. The two probes seem to be suitable for specific detection of catechol 2,3-dioxygenase sequences belonging to the *Pseudomonas* and *Sphingomonas* groups.
In the near future, the developed pairs of primers for PCR together with the oligonucleotides should be used for the detection of the initial dioxygenase and catechol 2,3-dioxygenase sequences in environmental samples to monitor the potential for PAH degradation without time-consuming cultivation.

Wikström, P., Wiklund, A., Anderson, A.C. and Forsman, M. (1996) DNA recovery and PCR quantification of catechol 2,3-dioxygenase genes from different soil types, J. Biotechnol. 52, 107-120.

EXPERT SYSTEM FOR SOIL REMEDIATION

R.H.P. Ringeling[1], A.G. Thomas[1], A. Honders[2]

[1] Subfaculty of Applied Earth Sciences, Delft Univ. of Tech., Mijnbouwstraat 120, 2628 RX Delft, The Netherlands
[2] NV Service Centrum Grondreiniging, Europalaan 250, 3526 KS Utrecht, The Netherlands

Keywords: Characterization, computer model, contaminated soil, databases, heavy metals, mineral oil, monitoring, PAH, soil washing.

INTRODUCTION

Recent changes in the Dutch legislation concerning the cleaning of contaminated soil have had a great impact on contaminated soil handling. It is now possible to reuse partially cleaned soil which under the former legislation would otherwise have to be dumped because it was not multifunctional. The new legislation "Bouwstoffenbesluit" (Construction Materials Mandate), which is supplementary to current legislation, defines the conditions for the environmentally balanced use of cleaned soil in building projects. However, for the application of cleaned soils in building projects, the material properties are also important. Thus it is necessary to check whether these properties change as a result of cleaning.

In order to provide the soil cleaning industry with a method to evaluate the new opportunities for cleaned soil with respect to the revised legislation, a two-phase project has been started to develop an expert system. The first phase consisted of collecting relevant data, while the second phase consisted of the development of the expert system. In this paper an overview of the first phase of the project will be given.

A relevant selection of soil samples and industrial processing routes had to be made to serve as a basis for the data collection. About 20 different Dutch soils were selected and characterized. Treatment at the soil cleaning plants was monitored by taking samples before and after each unit operation and analyzed on the basis of chemical and physical properties. The same unit operations were also tested on lab scale in order to establish the correlation with the industrial cleaning processes.

CHARACTERIZATION

The characterization focused on both the chemical and physical properties of the selected soils. The history of each soil was established to act as a reference for the interpretation of the characterization results, which is dependent upon the occurrence of the contaminant. The chemical properties included the determination of the contamination concentrations and the distribution of the contamination over the particle size ranges. Sink-float analyses were also performed to determine the occurrence of the contamination: as separate particles or adsorbed to the sand grains. The physical properties characterization included the measurement of organic matter content, percentage passing 63 microns and the particle size distribution of the samples.

The history of the selected soils varied, although the contamination was typically a mixture of polyaromatic hydrocarbons (PAHs), mineral oils and heavy

metals. Examples of the sites are: gas factories, car disassembly locations (scrap yards), chemical washing installations, leaking oil or gas tanks and depots/storage yards. Most of the soils were determined to be heavily contaminated, although a few lots were only moderately polluted. The contamination level was determined according to the intervention values as given in the Dutch soil protection law "Wet Bodembescherming".

The organic matter content of the selected soils varied from 0.5 to 6.6 wt%, while the percentage <63 μm varied from 2.2 to 25.5 wt%. In Figure 1 the range of the particle size distribution for the different soils prior to processing is indicated by the light gray area (Feed), within which the dark gray area shows the range for the cleaned soil products.

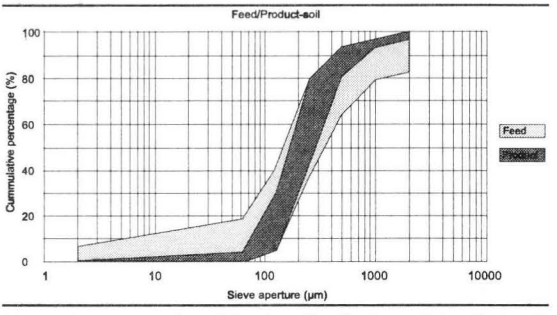


Figure 1. Range of particle size distribution of the feed soils and products.

PROCESSING ROUTES

In total, 11 process configurations were tested, ranging from the most simple combination of a screen and cyclone, to complex routes including scrubbing, flotation, low or high intensity magnetic separation, an upstream column or various spirals. The results of primary concern were the concentration reduction and change in physical soil properties.

The tests clearly demonstrated that at least one process step in addition to the basic screen and cyclone is necessary to clean heavily contaminated soil to meet the standards for use without restriction. The basic screen and cyclone combination failed in all cases to reduce heavily contaminated soils to under the category I standards, irrespective of the percentage of organic matter or <63 μm fraction. The process routes that included flotation and high gradient magnetic separation yielded the best cleaning efficiencies.

The organic content of the products of all process routes tested was under the 3 wt%, the maximum acceptable level for use of the soil in construction projects. Depending on the application, the maximum allowed percentage of material passing 63 μm is either 2 or 5 wt%. Except for the most simple screen/cyclone combination, all process configurations yielded products with less than 2 wt% passing 63 μm. The various process configurations all have the same effect on the particle size distribution of the products (refer to Figure 1).

CONCLUSIONS

The results of the first stage of the project are very promising for the success of the expert system currently under development. Collected data were consistent with expectations both for the characterization and cleaning results. This will support the correlation of parameters for laboratory and industrial results and it indicates that such an expert system will be successful in practical application.

IN-SITU BIOREMEDIATION: INCREASE OF EFFECTIVITY BY THE ADDITION OF HUMIC ACIDS

Werner Kördel, Helmut Klöppel and Kerstin Hund

Fraunhofer Institut for Environmental Chemistry and Ecotoxicology,
D-57377 Schmallenberg

Key words: in-situ remediation, PAHs, hydrocarbons, leaching behaviour, DOC, DHS from composts

Introduction

It is well documented that aqueous solutions of dissolved humic substances (DHS) increase the solubility of poorly soluble organic contaminants [Wahle and Kördel, 1997, Rebhun et al., 1996, Kördel et al., 1997). The DHS, through hydrophobic binding of organic contaminants, reduce their sorbability and facilitate desorption and remediation. After penetration through the soils the DHS which is loaded with contaminants can easily be coagulated - precipitated and separated by press-filtration. A further advantage of DHS is their availability and inherent degradability. They are natural soil constituents and they can be used as carbon sources by microorganisms without stimulating the growth to an unwanted extend.

Experimentals and Results

Three soils contaminated with PAHS and hydrocarbons (oils) were used for the study. Laboratory colums (14 cm in diameter and 60 cm in length) were filled with the soils and percolated with the following eluents: nutrient solution, DHS from two different compost sources and detergent solutions. The solubilizing properties of DHS extracted from compost are shown by figures 1 and 2. Compost sources of different ages and thus different stages of humification were extracted by shaking with water in a compost/water ratio auf 1/4 (fresh weight basis). Figure 1 elucidates that the moleculare weight of the DHS increases with time, whereas the total concentration of DHS decreases due to the degradation of the easily degradable carbon sources. Figure 2 shows that the solubilizing properties of DHS increase when DHS contains more components of high molecular weight. The solubilizing properties are the more pronounced the lower the solubility of the pollutants is (water solubility: phenanthren = 1000 µg/l; pyrene = 132 µg/l). The results of the ongoing experiments will give a comparison of the different eluents and their applicablility in field experiments.

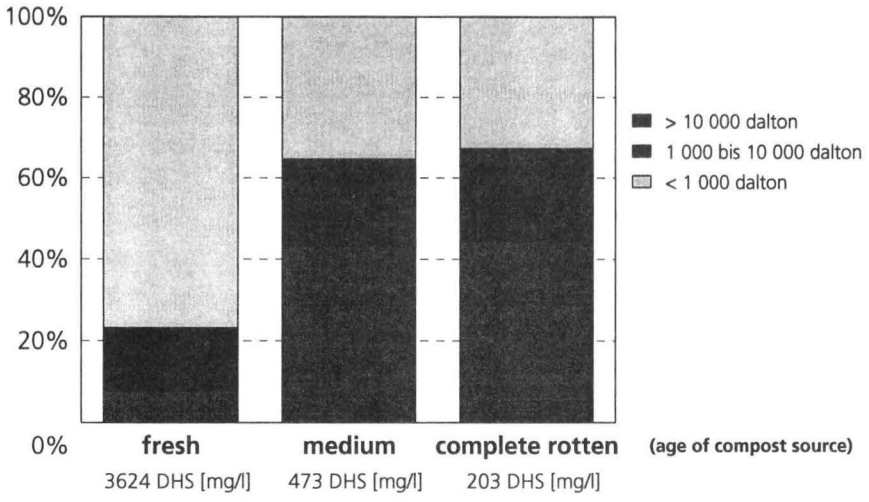


Figure 1.
DHS content and molecular weight of compost extracts

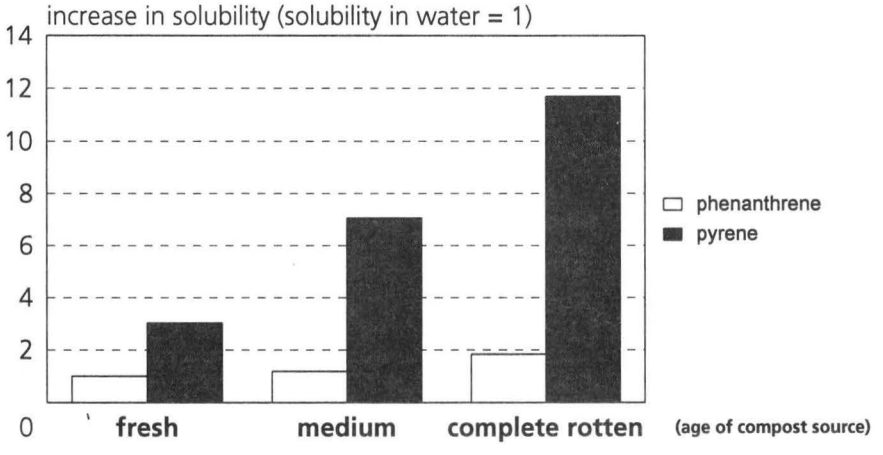


Figure 2.
Solubilizing properties of DHS

References

Rebhuhn, F. de Smedt and J. Rewatäbula (1996): Dissolved humic substances for remediation of sites contaminated by organic pollutants. Binding-desorption model predictions. Wat. Res., Vol. 30, 2027-2038

Wahle, U. and W. Kördel (1997): Development of analytical methods for the assessment of ecotoxicological relevant soil contamination - Part A - Development and Improvement of soil extraction methods for the determination of the bioavailable parts of contaminants, Chemosphere, Vol. 35, Nos. 1/2, 223-237

FIBER-OPTIC IN-SITU MONITORING SYSTEM FOR ORGANIC CONTAMINANTS IN WATER

J. Bürck, M. Mensch, K. Krämer, Forschungszentrum Karlsruhe, Institut für Instrumentelle Analytik (IFIA), P.O. Box 3640, D-76021-Karlsruhe, Germany

Key words: Fiber-optic sensor technology, in-situ measurement techniques, chlorinated hydrocarbons, BTEX, hydrocarbons, groundwater monitoring, waste waters, field test.

SUMMARY
The prototype of a portable infrared absorption fiber-optic sensor system for monitoring apolar hydrocarbons (HCs) in contaminated groundwater or industrial waste water is presented. This sensor system provides an HC sum concentration signal and can be used for continuous in-situ analysis in a broad concentration range from around 200 ppb up to a few 100 ppm. Field tests with the sensor system have been successfully performed.

INTRODUCTION

The environmental impact of hydrocarbon (HC) leakage and spills that contaminate soil and groundwater at former industrial sites is a problem world-wide. Discontinuous batch sample collection followed by laboratory analysis often is too time consuming and expensive, and can only provide a brief, temporary 'snapshot' view of the contamination. Due to this, there is a need for continuous in-situ HC screening and monitoring measurements in groundwater of contaminated areas, and in discharged process waters of industrial production and storage facilities or remediation systems, to meet regulatory discharge limits for HC contaminants.

In recent years new infrared spectroscopic sensing techniques are promising to fulfill these requirements. They combine the enrichment of apolar HC molecules in the hydrophobic polymer coating of an optical fiber with the direct absorptiometric measurement of the extracted species in the polymer, by using the evanescent wave of the light conducted in the fiber core [1]. The evanescent light penetrating into the cladding is absorbed at the C-H overtone absorption bands of the extracted organic species. This absorption, which is correlated to the HC concentration, can be measured by a spectral evaluation unit adapted to the sensing fiber. With this sensing principle, interference from broad water OH absorption bands or turbidity in the solution is avoided. The evanescent field absorption (EFA) sensor system developed in our institute consists of a quartz glass fiber sensing element with a silicone cladding and a photometer unit.

SENSOR SYSTEM SEPCIFICATIONS

The compact, cylindrical sensor element (14*5 cm in size) is built from an optical fiber with a sensing length of 12-30 m, which is coiled on a stainless steel/Teflon support. It is connected by all-silica fibers of up to 100 m length to a low-cost, portable near-infrared filter photometer. The sensing fiber with a core diameter of 210 µm is protected against mechanical damage by an outer stainless steel perforated plate casing. The photometer provides a sum signal of the HC compounds extracted by the sensing fiber, by measuring the integral absorption at the saturated and unsaturated C-H 1. overtone bands. The absorbance calculated by the microcontroller of the instrument is linearly dependent on the HC concentration. Up to 20 HC calibration functions can be stored on the microcontroller. The slope of the calibration function is dependent on the HC mixture and has to be determined experimentally. The HC concentration value is calculated directly by the microcontroller and indicated on the LCD display of the photometer. This stand-alone instrument can be easily operated by simple function keys. Signal zero-point setting is performed with the sensor in pure water. Afterwards, periodic measurements are started (minimum interval

is 15 s) and the sensor is contacted with the aqueous HC solution. Data are collected and stored automatically by the system. By way of an RS232 interface, stored data can be sent to a computer for evaluation and documentation purposes or new calibration data can be transmitted from the computer to the photometer. Temperature effects on the sensor signal are described by polynomial functions, which are stored on the microcontroller of the instrument. Thus, an automatic compensation of absorbance off-set signals due to temperature changes in the sample solution is obtained by measuring the temperature with a thermistor attached to the sensor.

The limits of detection for HCs typically are in the low ppm range. Recently, the values have been improved to a few 100 ppb, by adapting the photometer to a 30-m sensing fiber. The time for measuring an aqueous HC solution usually is in the range of 2-15 minutes. The enrichment of volatile hydrocarbon molecules (e.g., chlorinated HCs, BTEX) in the silicone cladding is completely reversible. For long-chain HC molecules, contained in diesel fuels or mineral oils the sensor has to be regenerated by rinsing with petroleum ether or acetone.

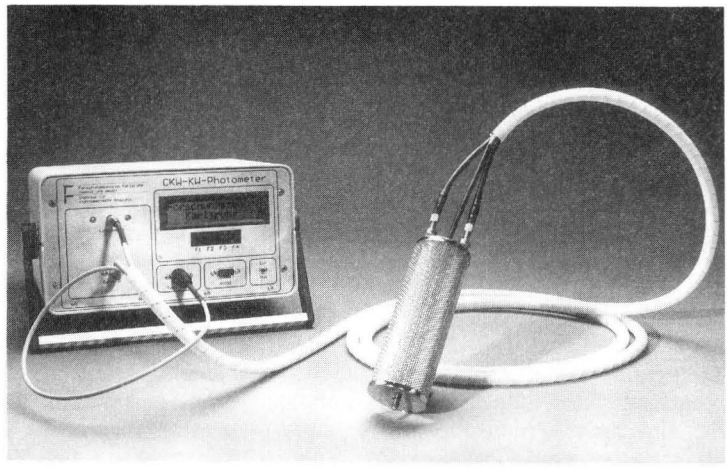


Figure. 1. Photograph of fiber-optic EFA sensor/photometer in-situ monitoring system for apolar hydrocarbons in water.

FIELD TESTS

The feasibility of in-situ chemical sensing of apolar hydrocarbons with the EFA sensor/filter photometer system has been demonstrated in field-trials. Continuous in-situ measurements in an artificial aquifer at the VEGAS research facility and with trichloroethene (TCE) as single pollutant showed, that the sensor system provides quantitative data over a measuring period of some weeks without re-calibration, and a mean deviation of 9 % compared to off-line analysis has been obtained. The sensor fiber proved to be chemically stable even in the presence of 'free' TCE phase.

During field experiments at the remediation facility of the former chemical landfill Mühlacker, process water contaminated with different chlorinated hydrocarbons in the low ppm concentration range was monitored, with the sensor being calibrated for the typical analyte composition in the HC mixture. For the sum concentration given by the sensor system an acceptable mean deviation of around 20 % compared with the HC sum concentration measured by GC reference analysis was obtained. However, these measurements also revealed, that reasonable determination without frequent re-calibration of the system can only be obtained, if the ratio of the main compounds in the HC mixture stays constant within certain limits. If stronger changes in the analyte composition occur, the sensor still traces the changes in concentration, but can only provide semi-quantitative data due to the fact being calibrated with an invalid calibration function.

1. Sensfelder, E., Bürck, J. and Ache, H.J.(1996) Determination of hydrocarbons in water by evanescent wave absorption spectroscopy in the near-infrared region, *Fresenius J. Anal. Chem.* 354, 848-851.

Soil pollution - mass spectrometry contribution in qualitative and quantitative approaches.

PM Dudermel, S Dupeyron, D Couturier

Laboratoire d'analyse de micropolluants organiques, Departement Eaux - Environnement, Institut Pasteur de Lille, 1, rue du Professeur Calmette, BP245, F-59019 Lille Cedex, France
Phone (33) 320 87 73 63, Fax (33) 320 87 73 83

Key words: analytical method, gas chromatography, mass spectrometry, screening, contaminated soil

Organic micropollutants liable to contaminate soils present two fundamental characteristics :

- they belong to all known chemical families, describing a wide range of molecules,
- they cover a wide range of concentration from few micrograms per kilograms of earth to several hundreds of milligrams per kilo of studied soil.

Despite the varying nature of the possible contaminants and in order to answer to the specifications of soil remediation, it is necessary to develop an analytical strategy to assess the contamination of these matrices as accurate as possible.

The use of numerous specific methods gives no global vision of the contaminant nature. It generally involves significant increase in the analytical cost, inconsistent with the demands of pollution studies (treatment of a high number of samples, fast delivery of results, assessment of the real contamination).

The use of mass spectrometry can contribute to the identification of the analyte, even without owning the analytical standard. The identification procedure includes several steps (Figure 1), well-known to be delicate. For example, during the acquisition of the mass spectrum, the choice of the spectrum limits is essential for the identification test efficiency. The subtraction of the background noise from the unknown mass spectrum is also an influential parameter.

The quantitative approach is based on the response factor of the nearest known compound (reference peak) and allows to estimate individually concentration of detected compounds (unknown peaks).

The major points of this method are :

- an extensive control of the signal identification algorithm,
- a quantitative approach as faithful as possible. Thus, regarding the lack of available standards, this procedure is well designed to produce data for all kind of unknown compounds,
- a low cost of analysis according to the amount of information provided.

Contaminated Soil '98, Thomas Telford, London, 1998, 913–914

The screening method by mass spectrometry that we purpose here, is an efficient tool for the drawing up of a contamination statement and for the supervision of clean up processes (Table 1). It could also steer the analytical monitoring to more specifics techniques. Finally, it could be adapted to industrial wastewater and contaminated groundwater studies, after modification of the sample preparation procedure (Table 2).

Table 1 : Limits of quantitation (mg/kg) for soil studies.

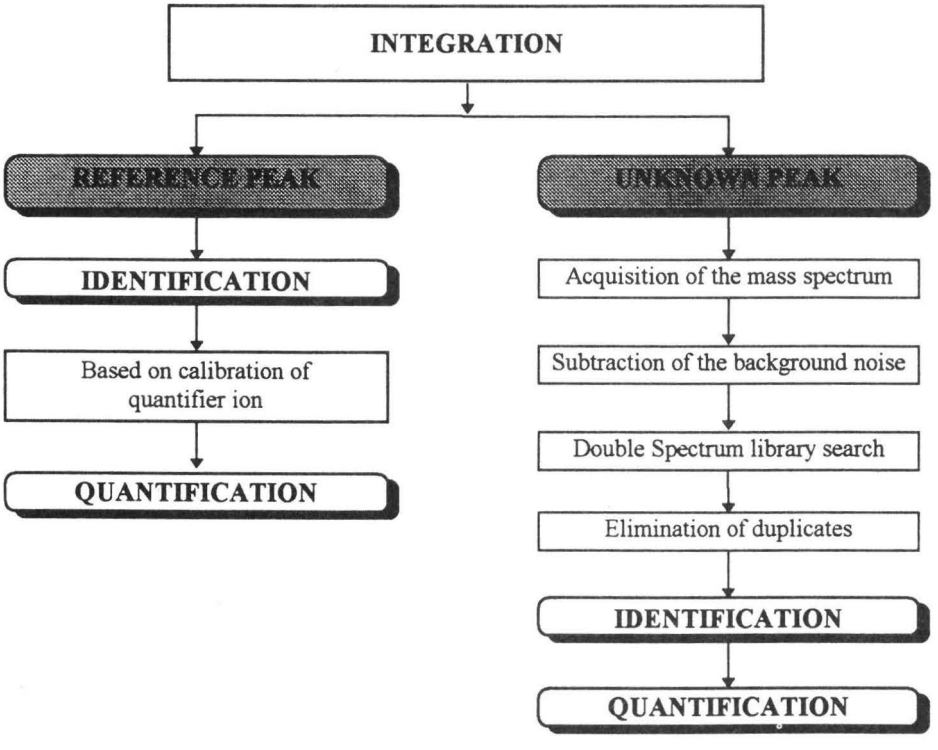
	Screening MS	Specific methods
PAH	0.05	0.005
PCB/OCC	0.05	0.001
Others	0.05	0.05

Table 2 : Limits of quantitation (µg/L) for contaminated water.

Screening MS	1
Screening Phenols	0.5 - 1
Screening Volatile	0.5 - 1

Further studies are in progress to perform other techniques of MS screening such as GC/NCI/MS screening and LC/MS screening for more polar compounds.

Figure 1 : Identification procedure.



OCCURRENCE OF POLYCHLORINATED DIBENZO-*p*-DIOXINS AND DIBENZOFURANS AS IMPURITIES IN WOOD PRESERVATIVE CONTAMINATED AND REMEDIATED SOIL.

K. Kalevi[1], A. Donner[1], H. Kiviranta[2], T. Vartiainen[2], K.S. Jørgensen[1]

[1]Finnish Environment Institute, P.O. Box 140, FIN-00251 Helsinki, Finland
[2]National Institute of Public Health, P.O. Box 95, FIN-70701 Kuopio, Finland

Keywords: contaminated soil, dioxins, bioremediation, soil clean-up

Spills and work with wood preservatives have been the reason for contamination of many sawmills and wood impregnation plants around the world. In Finland a commercial chlorophenol mixture, Ky 5, has been generally used for more than 40 years. It was completely banned in Finland in 1988. Chlorophenol formulations are still used in other countries for e.g. wood, cotton and leather preservation. The chlorophenols inhibits fungal attack and staining of the wood. The chlorophenol formulation Ky 5 was, however, not very pure, and impurities of polychlorinated biphenyls (PCBs), polychlorinated phenoxyphenols (PCPPs) and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) have later been detected in the pure formulation as well as in contaminated soil (Kitunen et al. 1987; Vartiainen et al. 1995). These compounds have not, however, been routinely measured in site investigations mainly due to the complexity and expensiveness of analysis.

Due to the solubility and mobility of chlorophenols, they have often been found to contaminate groundwater and the general public concern has been directed towards the chlorophenols due to their acute toxicity. Even though PCDD/Fs are some of the most toxic compounds, they do not exhibit acute toxicity and they are very tightly bound to particles and do not leach. During the 1980s the contaminated sites in Finland were registered and remediation of around 50 sawmill sites have been remediated during the late 1980s and in the 1990s with regard to chlorophenols. Around 500 sites are still to be cleaned up. Many sawmills are located on lake or river shores, due to earlier transportation of wood on the waterways. Typically old sawmills are situated in the centre of smaller towns, and in many cases the areas are attractive for housing.

The most common remediation methods in Finland for chlorophenol-contaminated soil has been composting in biopiles off or on site. To a lesser extent soil has been isolated on landfills or thermically treated. The bioremediation technology has worked out excellent with regard to chlorophenols (Laine and Jørgensen, 1997). After the completion of many remediation events it has become evident that extremely high concentrations of PCDD/Fs can still be found. The purpose of this study was to thoroughly investigate the presence of PCDD/Fs at 5 sites that were remediated with regard to chlorophenols with state support from 1988 to 1996. The investigation covered both bioremediated soil and what might be left on the original site.

PCDD/Fs were analyzed by high resolution mass spectrometry (HRGC/HRMS) and chlorophenols were analyzed by GC-ECD. The preliminary results are given in Table 1. The main components of the PCDD/Fs are PCDFs (usually more than 98 %) and mainly hexa-, hepta-, and octa-chlorinated. The results are given as international 2,3,7,8-TCDD toxicity equivalents (I-TEQ). The target value in Finland for remediation actions is 500 ng/kg I-TEQ, and the limit value for non contaminated areas is 20 ng/kg I-TEQ. The values recorded in this study exceed the remediation target value with up to 26 times and the limit value for non-contaminated soil with up to 370 times. The high concentrations in the bioremediated soil is due to the original presence of the PCDD/Fs in the chlorophenol contaminated soil and the results show that in most cases very little PDCC/Fs remained at the sites. Recent studies have confirmed that no biological formation of PCDD/Fs from chlorophenols occurs in this type of bioremediation (Laine et al., 1997)

The appearance of these high concentrations of PCDD/Fs requires important decisions for the land use and for the remediation technologies to be used. Before that can be done a very thorough risk evaluation both with regard to the exposure to humans and to the environment has to be carried out.

Contaminated Soil '98, Thomas Telford, London, 1998, 915–916

We need decisions for both sawmill areas that have already been remediated with regard to chlorophenols, and for all the sawmill areas, where both chlorophenols and PCDD/Fs are present, which may be an even bigger problem. Today there are very few remediation technologies available for the removal of PCDD/Fs, only very expensive incineration or isolation at hazardous waste landfills seem to be safe methods at the moment, so here is a great challenge for remediation technology developers.

Table 1. Examples of levels of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and chlorophenols in bioremediated sawmill soil and in soil left at the remediated areas.

Sampling site	PCDD/Fs		Chlorophenols (Sum of di-, tri-, tetra- and penta-) mg/kg dry wt
	Total amount ng/kg dry wt	I-TEQ[a] ng/kg dry wt	
Site 1			
Remaining soil at site	33	3	0.47
	16	0.2	0.76
	1 450	19	0.27
	1 030 000	3 680	0.19
	95 200	277	2.01
Nonremediated soil (off site)	1 744 000	7 278	
	15 947 000	221 000	27.3
	25 425 000	415 000	59
	141 100 000	1 954 000	108
Lake sediment off the saw mill area	2 980	21	0
	1 060 000	2 820	0
Site 2			
Bioremediated soil (off site)	99 900	503	
	193 000	809	2.52
	105 000	463	
Remaining soil at site	451	2	
	423	3	
	201	1	
Site 3			
Bioremediated soil (off site)	4 100 000	13 000	1.94
	3 150 000	10 800	2.91
	3 210 000	10 400	6.06
	3 280 000	12 100	3.09

[a] I-TEQ: International 2,3,7,8-TCDD toxicity equivalence

References

Kitunen, V.H., R.J. Valo, and M.S. Salkinoja-Salonen (1987) Contamination of soil around wood-preserving facilities by polychlorinated aromatic compounds. *Environ. Sci. Technol. 21, 96-101.*

Laine, M.M., J. Ahtiainen, N. Wågman, L.Öberg, and K.S. Jørgensen. (1997) Fate and toxicity of chlorophenols, polychlorinated dibenzo-p-dioxins and dibenzofurans during composting of contaminated sawmill soil. *Environ. Sci. Technol. 31, 3244-3250.*

Laine, M.M. and K.S. Jørgensen. (1997) Effective and safe composting of chlorophenol-contaminated soil in pilot scale. *Environ. Sci. Technol. 31, 371-378.*

Vartiainen, T., R. Lampi, K. Tolonen, and J. Tuomisto. (1995) Polychlorodibenzo-p-dioxin and polychlorodibenzofuran concentrations in lake sediment and fish after a ground water pollution with chlorophenols. *Chemosphere 30, 1439-1451.*

Rapid procedures for the on-site measurement of polycyclic aromatic hydrocarbons in soils from former gasworks

Bennett, A.M.A., Jones, S.D. and Morris, R.S.

Environmental Services, BG Technology, Gas Research & Technology Centre, BG Plc., Ashby Road, Loughborough, Leics. LE11 3GR

Key words: field test; polycyclic aromatic hydrocarbons; gasworks; soil

Introduction

Polycyclic aromatic hydrocarbons (PAH) are one of the main sources of the environmental liability associated with former gasworks. Current measurement strategy is for soil samples to be packaged and sent for measurement of the concentrations of these contaminants at off-site laboratories. Decisions on the quality of the soil, and hence its ultimate fate, are therefore delayed. Measurement in the time-frame of on-site construction activities would circumvent this problem and decrease costs.

BG plc has an established development programme to move the measurements involved in site assessment into the operational time-frame and to decrease the cost whilst maintaining the quality. Here, rapid procedures for the on-site measurement of PAH in the soils from former gasworks are described.

Method development

Soils were sampled at a number of former gasworks in the U.K. Laboratory analytical procedures followed the protocol defined by BG Property Division [1] for site assessment . Material for measurement via both procedures was obtained from the same sample. Methanol was used as the extraction solvent. Optimum conditions for ultrasonic extraction were determined by variation of the soil/solvent ratio in the range 1 to 25 and variation of the extraction period in the range 1 to 30 mins. A sub-sample of this extract was filtered (0.45 μm) and diluted with methanol, if required, before analysis by gc-FID. Figure 1 shows the correlation between ultrasonic extraction with methanol and soxhlet extraction with cyclohexane. Forty-eight contaminated soils from 16 former gasworks were treated to produce the correlation.

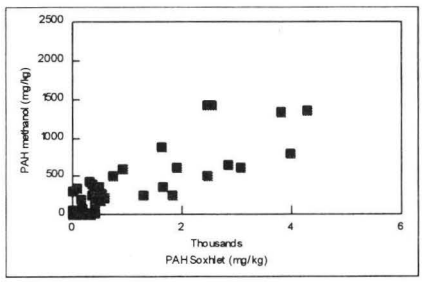
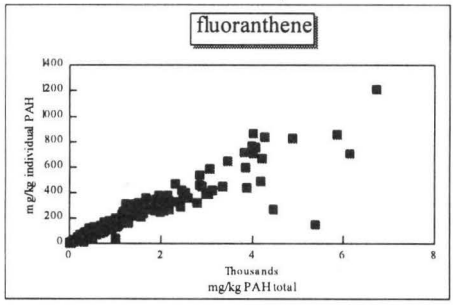


Figure 1: methanol extraction = 0.277 +/-0.029 soxhlet extraction + 90

For PAH concentrations up to about 4,500 mg/kg a positive correlation ($r = 0.83$) significant at $p = 0.99$ exists between the two extraction procedures. Linear regression gave the equation above.

The distribution of PAH in 286 contaminated soils sampled from 33 former gasworks was measured. Figure 2 demonstrates the consistency of composition for two PAH in these soils, fluoranthene and

pyrene. The correlation between the specific PAH and the total PAH is significant at p =0.99; r = 0.93 and 0.96, respectively. Linear regression gave the following regression equations.



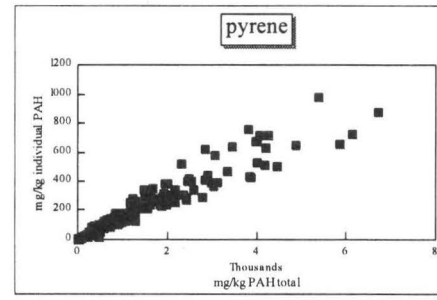


Figure 2: fluoranthene = (0.153+/- 0.0025)* total PAH: pyrene = (0.1474 +/- 0.0018) * total PAH

When excited by light energy in the wavelength range 300 to 410 nm, PAH fluoresce predominantly in the range 400 to 500 nm. Tests using fluoranthene in methanol and an excitation/emission pair of 410/450 nm showed that the Beer-Lambert law was obeyed in the concentration range 0-800 mg/l with a molar extinction coefficient of 1.24×10^5 $lM^{-1}cm^{-1}$. Fluoranthene was chosen as the test PAH because it is a major component of the total PAH in soils from former gasworks. Calibration (Figure 3) was conducted directly between the fluorescence intensity measured at 450 nm on wet soils and the total PAH concentration measured by gc-FID on soxhlet extracts. The correlation (r = 0.79) between fluorescence intensity and total PAH concentration is significant at p = 0.99. Linear regression of fluorescence intensity on total PAH concentration gave the regression equation below.

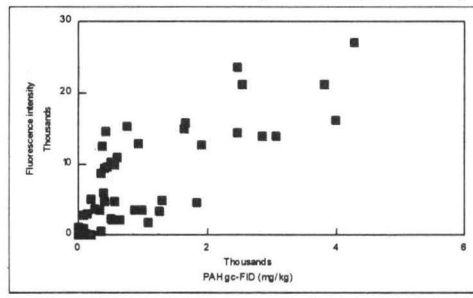


Figure 3: Fluorescence intensity = (4.97 +/- 0.58) * total PAH + 2725

Combination of the regression equations for the extraction and detection stages of the procedures above yield a single mathematical expression that describes the conversion of a measurement procedure based on ultrasonic extraction and detection of a single PAH to the same basis as exhaustive soxhlet extraction followed by gc-FID for all 16 PAH defined by the US EPA.

Method Performance

Precision tests of the chromatographic procedure measuring pyrene and using 11 replicates of a contaminated soil gave a relative standard deviation at 95% confidence of 4%. For the fluorescence procedure, precision tests using 11 replicates of a contaminated soil containing 858 mg/kg and 5567 mg/kg gave relative standard deviations at 95% confidence of 8% and 13%, respectively.

Operating costs, bench-marked against the laboratory procedure show that the fluorescence and chromatographic procedures are 75% and 60% cheaper, respectively and deliver measurement data within 20-30 minutes after sampling.

References : [1] "Guidance for assessing potential contamination on gasworks sites", BG Property Division, Basingstoke, U.K., 1997.

BIODEGRADATION OF METHYL t-BUTYL ETHER BY A MIXED BACTERIAL CULTURE.

D. Corcho[1], J. D. Linton[2], R. J. Watkinson[1] and D. Lerner[1]

1 Civil and Structural Eng., Univ. of Sheffield, Mappin Street, Sheffield S1 3JD, U.K
2 Shell International Oil Products, Amsterdam, Netherlands

Key words: bacteria, co-oxidation, groundwater, microbial degradation, MTBE, organic contaminants

SUMMARY

Methyl *tert*-butyl ether (MTBE) is a widely used additive in gasoline. It is found in groundwater and has been thought to be non-biodegradable. However our studies have demonstrated the potential for microbial degradation. A mixed culture CH1 exhibits a co-oxidation system where the organisms utilise cyclohexane for carbon and energy but co-oxidise MTBE. This culture will also co-oxidise other organic contaminants such as TAME or phenol. Respirometric experiments have been conducted to evaluate biodegradation kinetics with these oxygenates and related hydrocarbons substances. These experiments have demonstrated production of *tert*-butyl alcohol (TBA) by the co-oxidation system and a possible inhibition of the cell activity by this intermediary metabolite.

Petroleum oxygenates have been used for 10 years to improve gasoline combustion and thereby reduce carbon monoxide emissions. The most commonly used oxygenate is methyl tertiary-butyl ether (MTBE), which is very mobile in groundwater because of its solubility (48 g/L). MTBE has been detected in storm water and in groundwater (Squillage *et al.*, 1996). Earlier studies indicated that MTBE is not biodegraded aerobically (Fujiwara *et al.*, 1984) or anaerobically (Suflita and Mormile, 1993). However, others (Salinitro *et al.*, 1994) have demonstrated MTBE biodegradation to biomass and CO_2 by a mixed culture. The present study examines the possibility that cyclohexane-utilising organisms can oxidise MTBE and related alkyl ethers.

The cyclohexane-utilising bacterial culture (CH1) used in this study was taken from a continuous culture run with cyclohexane as the sole source of carbon and energy. The mixed culture contains 4 different bacterial species, the predominant cyclohexane utiliser and three other organisms. It is thought cyclohexane it is oxidised via a mono-oxygenase system. Different concentrations of cyclohexane (0.015%, 0.15%, 0.35% and 0.75%) were added to liquid microcosms containing mineral media in order to study the effect of substrate concentration on the growth of CH1. The results showed after 6 days of incubation an increase in the final CH1 cell density with increasing cyclohexane concentration, and absence of substrate inhibition over the range of cyclohexane concentrations studied. Two incubation temperatures (25°C and 37°C) were used to study the temperature effect on the CH1 culture growth. The CH1 growth rate observed at 37°C was twice that at 25°C.

In respirometric experiments in a Clark cell, washed cell suspensions of CH1 culture were found to oxidise cyclohexane and cyclohexanol readily but not carbohydrates such as

glucose and fructose, nor amino acids such as glutamic acid. A range of other organic compounds were oxidised including MTBE (Table 1).

Table 1. Respiration rates of a range of organic compounds by washed cells from the CH1 culture grown on cyclohexane.

Compound	cyclohexane	cyclohexanol	MTBE	TAME	phenol
Substrate conc. (mg/l)	13.7	10.0	11.0	3.7	23.0
Relative resp. rate (%)	100	135	35	17	45

The effect of MTBE on the kinetics of cyclohexane oxidation by CH1 was measured in the Clark cell respirometer. Lineweaver-Burk plots of the respiration rates with and without MTBE showed a competitive effect of MTBE on the cyclohexane oxidation. MTBE may be competing directly with cyclohexane at its binding site on the mono-oxygenase system.

Products of MTBE oxidation by CH1 were determined by GC analysis. MTBE was converted into a single product that accumulated and was not metabolised further. The metabolite had the same retention time as *t*-butanol and this identity was confirmed by GC-MS. Experimental data indicates that *t*-butanol may have an inhibitory effect on the culture activity, however more work is required to prove this hypothesis.

This paper shows the capabilities of a cyclohexane-utilising culture to oxidise MTBE. Experimental evidence suggests that the oxidation was mediated via a cyclohexane mono-oxygenase since MTBE was a competitive inhibitor of cyclohexane oxidation. MTBE was converted into a single product identified as *t*-butanol, which was not metabolised further. The cyclohexane-utilising culture can oxidise other organic compounds such as TAME, cyclohexanol and phenol.

REFERENCES

Fujiwara, T., Kinoshita, T., Sato, H., and Kojima, I. (1984) Biodegradation and bioconcentration of alkyl ethers. *Yukagaku* 33:111-114.

Salinitro, J. P., Diaz, L. A., Williams, M. P., and Wisniewski, H. L. (1994) Isolation of a bacterial culture that degrades methyl *t*-butyl ether. *Appl. Environ. Microbiol.* 60:2593-2596.

Squillage, P. J., Zogorski, J. S., Wilber, W. G., and Price, C. V. (1996) Preliminary assessment of the occurrence and possible sources of MTBE in groundwater in the United States, 1993-1994. *Environ. Sci. Technol.* 30: 1721-1730.

Suflita, J. M., and Mormile, M. R. (1993) Anaerobic biodegradation of known and potential gasoline oxygenates in the terrestrial subsurface. *Environ. Sci. Technol.* 27:976-978.

„Chemical speciation of organic and inorganic compounds in municipal waste incinerator residues"

R. Köster

Forschungszentrum Karlsruhe, Institut für Technische Chemie/ Bereich Wasser - und Geotechnologie

D 76021 Karlsruhe, P.O. Box 3640, Germany

Phone 07247 822302, fax 07247 822246, e-mail rainer.koester@itc-wgt.fzk.de

With about 3 mio Mg/a, slags make up the main fraction of solid residues of municipal waste incineration plants in Germany. The environmental relevance when used again e.g. in civil engineering or road construction is mainly determined by the mobilization behaviour of the slag pollutants. Of particular interest are heavy metals, as their concentrations exceed those of the lithosphere by 10 - 10^3. Special attention is paid among others to copper. Due to binding of Cu to proteins, it may have a toxic effect even to man when its concentration in food is too high [1]. The mobilization behaviour of copper can in principle be influenced by complexation reactions e.g. with residual organic contaminations of the slag.

By means of TRFA and ICP-AES, it was possible to identify Si, Al, Ca, Mg, Fe and O as main slag constituents, Ti, Cr and Cu as side constituents and Co and Ni as trace elements. The copper inventory of the slags amounts to 0.1 - 0.3 wt.%. Mineralogical characterization of the phase mixture by transmitted light microscopy and XRD yields quartz, calcite, anhydrite, melelithe and new glass phases formed by incineration as main constituents.

The DEV S4 test serves as a basis for studying the mobilization of copper from waste incineration slags. Eluated copper is determined by AAS and ICP-AES as a function of elution time. The results show a maximum of ≈ 90 µg Cu/l after 2 - 4 hours. After 50 - 60 hours, copper concentration of the eluate amounts to 20 - 35 µg/l and varies only slightly. The pH value of the eluate is about 12. Maximum copper concentration of the eluate is below the value of 0.1 mg/l given by the EC regulation [2].

Cu eluate concentrations are confirmed by geochemical model calculations based on the solubility of the CuO which is detected in the slags. Solubility of CuO as a function of the pH value is calculated taking into account hydroxyl complexes. The calculations exhibit an increase in solubility by 10^3 when the pH value is shifted to the neutral or slightly acid range. Besides the elution behaviour, the pH-determining parameters such as the acid neutralization capacity (ANC) of the slags and the respective background, the influence of the organic residual components on the ANC and the "acid rain" are of crucial importance for evaluating the long-term environmental compatibility. To understand the long-term mobilization behaviour, the copper speciation, i.e. the types of copper bonds in the existing slag phase mixture with an incongruent solution behaviour must be known. Three characterization methods are applied for Cu speciation:

-Sequential extractions
-Density fractionation for Cu phase enrichment
-Solid state/surface analysis methods (light microscopy, X-ray diffraction studies, electron microprobe analysis and XPS).

The following Cu phases can be identified:
-Cu^0, CuO, Cu_2O
-Cu in metal alloys
-Alkaline Cu carbonates such as malachite $CuCO_3 \bullet Cu(OH)_2$ and azurite $2CuCO_3 \bullet Cu(OH)_2$ (as weathered products following the removal of the slag from the wet discharging system of the waste incineration plant).

A detailed characterization of the carbon-containing constituents of fresh and deposited slags from waste incineration is performed with particular consideration of organic

compounds. Total carbon contents vary between 1 and 2.5 wt.%. C can exist in 3 basically different forms: inorganic carbon (carbonates, carbides), elementary carbon (black carbon) and/or organically bound carbon. Inorganic carbon is determined after acidification of slags as CO_2. The differentiation of organic and elementary carbon is based on the thermal desorption of the organic substances in inert atmosphere, followed by an oxidation with air to CO_2 with subsequent IR detection. The total of organic and elementary carbon is determined by oxidation to CO_2 in air.The inorganic carbon fraction is ≈60% of the total carbon content. The organic fraction amounts to ≈10%, the elementary fraction to ≈30% of the total carbon content. The carbonate/carbide fraction can be assigned mainly to the carbonates which are identified clearly by TG and DTA analyses.

Identification and determination of organic slag constituents are accomplished after soxhlet extractions with water and various organic solvents of decreasing polarity using GC-MS and HPLC technology. By means of these methods, the following organic compound concentrations (related to dry weight) can be detected in the waste incineration slags in addition to polycyclic aromatic hydrocarbons (PAHs) and dioxins/furans:

Organic compounds found in slags

Compounds	*Conc. [mg/kg]*	*Polar organic acids*	*Conc. [mg/kg]*
Alkanes	2.0	Oxalic acid	3
PAHs	0.1	Lactic acid	4
Fatty acids	30	Malonic acid	0.6
Phenols	0.4	Acetic acid	14
Phthalates	3	Adipic acid	10

(Based on analytical data obtained for three waste incineration slags)

Undecane, octadecane and nonadecane can be identified clearly. The PAHs detected consist of >10 individual substances with naphthalene and acenaphthene making up the main fraction. The fatty acids comprise more than 10 saturated fatty acids with palmitic acid reaching a proportion of more than 50%. Among the four phthalates identified, the main fraction is made up of di(2ethylhexyl)phthalate. This can be attributed to its wide use as a standard plasticizer of PVC plastics. Ongoing improved extraction techniques applying organic solvents, supercritical CO_2 and optimised GC-MS analysis in the EI and CI mode are aiming at identifying additional polar organic acids.

The findings obtained with regard to copper speciation allow to chemically understand the dissolution/saturation/conversion processes taking place in the complex waste incineration slag. It is also shown that a reproducible long-term evaluation of pollutant mobilization from waste incineration slags requires methods which model the current environmental conditions in a more realistic way than simple elution tests. The organic compounds identified are not expected to result in an environmental pollution when using the slags as a secondary material in civil engineering and road construction. On the basis of the organic compounds detected, possible decomposition reactions and their influence on the ANC and complexing reactions with heavy metals can be evaluated and future contamination may be prevented.

References:

[1] Summary Review on the Health Effects Associated with Copper, Springfield, VA:EOA 1987

[2] Richtlinie des Rates vom 15. Juli 1980 über die Qualität von Wasser für den menschlichen Gebrauch (80/778/EWG). Amtsblatt der Europäischen Gemeinschaften, 30. 8. 1980, Nr. L 229, S. 11 - 29

BACTERIAL BIOSENSORS TO SCREEN *IN-SITU* BIOAVAILABILITY, TOXICITY AND BIODEGRADATION POTENTIAL OF XENOBIOTIC POLLUTANTS IN SOIL

Y. Ferguson[1,2], E. Shaw[3], L. A. Glover[2], K. Killham[1] and A. A. Meharg[3].
[1,2] Dept. of Plant & Soil Science, and Molecular & Cell Biology, Univ. of Aberdeen, St. Machar Dr., Aberdeen. AB24 3UU, UK. [3]Inst. of Terrestrial Ecology, Monks Wood, Abbots Ripton, Huntingdon, Cambridgeshire. PE17 2LS, UK.

Key words: Biosensor, soil, xenobiotic, toxicity, bioavailability, biodegradation.

SUMMARY
lux-marked *P. putida* biosensor was a sensitive reporter of 2, 4-DCP toxicity and has shown potential for determining bioavailability, toxicity and biodegradation of this xenobiotic in soil pore classes.

INTRODUCTION
Soils are the major sink for chlorophenols (e.g. 2, 4-DCP) produced by industrial, agricultural and domestic processes. Traditional, chemical analyses of soil xenobiotic contamination provides no indication of bioavailability, toxicity of complex mixtures and breakdown products, or potential for biodegradation. Xenobiotic toxicity has been monitored in soil using luminescent (*lux*) - based bacterial biosensors (Paton *et al.*, 1997). *lux* bioassays are sensitive indicators of microbial metabolism. Toxicity of xenobiotics in soil to *lux*-marked bacteria will be affected by their physical location. White *et al.* (1994) showed that bacteria can be introduced into specific soil pore classes. Similarly, xenobiotics can be positioned into the same/different soil pore classes as bacteria. Spatial/temporal effects of xenobiotics toxicity and bioavailability in soil can, therefore, be determined *in situ* by combining *lux*-based bioassay and pore placement techniques. The aims of this paper were to construct and characterise a sensitive *lux*-marked biosensor for screening the *in-situ* toxicity of 2, 4-DCP in soil.

MATERIALS AND METHODS
luxCDABE genes were introduced into *Pseudomonas putida* (NCIMB 12708) via plasmid pUCD607 by tri-parental mating. Growth and luminescence of *P. putida* 12708 pUCD607 were determined during batch culture. Sensitivity of *P. putida* 12708 pUCD607 cells to a range of environmental pH values was investigated by luminometry, using pH adjusted double deionised water. Effects of cell activity and exposure time on toxicity of 2, 4-DCP standard solutions, to *P. putida* 12708 pUCD607 cells were also assessed by luminometry. In addition, toxicity of 2, 4 - DCP was compared between *P. putida* 12708 pUCD607 cells and resuscitated freeze dried *E. coli* HB101 pUCD607 cells, by luminometry. A preliminary study of 2, 4-DCP toxicity in autoclaved soil pores was performed. 2, 4-DCP was partitioned into 30 - 60 μm pore class as described by White *et al.* (1994). Soil samples were equilibrated to allow passive movement of 2, 4-DCP into specific soil pores and adsorption onto soil aggregates. Moisture content was re-adjusted to enable positioning of *P. putida* 12708 pUCD607 cells. Soils were equilibrated, then slurried and destructively sampled. Luminescence of contaminated and control soils was measured by luminometry.

RESULTS

Light output of *P. putida* 12708 pUCD607 cells was constitutive during growth and maximum light output was ~2 x 10^6 RLU in stationary phase (data not shown). Late logarithmic phase *P. putida* 12708 pUCD607 cells were sensitive to low pH values, but maximum luminescence was obtained between pH 5 and 8, which included pH values of soils used in this study (data not shown). Toxicity of 2, 4-DCP to *P. putida* 12708 pUCD607 following 15 min exposure, was affected by cell activity and stationary phase cells (growth phase 3) were least sensitive (Table 1). The EC_{50} of cells harvested in late logarithmic phase (growth phase 1) was not statistically significant ($p = 0.341$) from that of cells harvested in early stationary phase (growth phase 2; Table 1). Sensitivity of late logarithmic phase *P. putida* 12708 pUCD607cells to 2, 4-DCP was also determined by length of contact time and cells were most sensitive after 30 minute exposure (Table 1). Late logarithmic phase *P. putida* 12708 pUCD607 cells were statistically ($p < 0.001$) more sensitive to 2, 4-DCP than resuscitated, freeze dried *E. coli* HB101 pUCD607 (Table 1) cells following 15 minute exposure. Preliminary data showed that luminescence of *P. putida* 12708 pUCD607 cells exposed to 2, 4-DCP in the soil pore class 30 -60 μm was ~50 % of that in control samples (Table 1).

Table 1. Effective concentration (EC_{50}) which resulted in 50 % reduction (compared to control samples) of cell light output following exposure to 2, 4-DCP. Results are quoted as a mean ± standard error. Unless stated otherwise all bioassays were carried out in triplicate after 15 minute exposure using duplicate cell populations of late logarithmic phase cells.

	growth phase 1	**growth phase 2**	**growth phase 3**
EC_{50} (μg ml^{-1})	7.83 ± 0.56	8.43 ± 0.20	11.9± 0.68
	8 min exposure	**15 min exposure**	**30 min exposure**
EC_{50} (μg ml^{-1})	17.65 ± 0.72	7.47 ± 0.50	3.53 ± 0.07

	***P. putida* 12708 pUCD607**	***E. coli* HB101 pUCD607**
EC_{50} (μg ml^{-1})	7.3 ± 0.25	15.38 ± 0.23
	2, 4-DCP spiked soil	**control samples**
Light output (RLU)	2138.54 ± 48.25	4230.62 ± 671.17

CONCLUSION

A bright *lux*-marked *P. putida* strain was constructed, which had a wide pH tolerance and was very sensitive to 2, 4-DCP standard solutions at pH 7. Preliminary results indicate that this strain was also a sensitive *in-situ* indicator of 2, 4-DCP contamination in soil. Further work is currently being carried out to study effects of the spatial location of 2, 4-DCP in soil pores on bioavailability, using *P. putida* 12708 pUCD607.

REFERENCES

Paton, G. I., Rattray, E. A. S., Campbell, C. D., Cresser, M. S., Glover, L. A., Meeussen, J. C. L. and Killham, K. (1997). Use of genetically modified microbial biosensors for soil ecotoxicity testing, in Pankhurst, C. S *et al.* (eds). Soil health CAB International, pp. 397-418.

White, D., FitzPatrick, E. A. and Killham, K. (1994). Use of stained bacterial inocula to assess spatial distribution after introduction into soil. *Geoderma 63, 245-254.*

CHROMIUM CONTAMINATION CLEAN UP USING ORGANIC WASTE MATERIALS

H J Duncan and T H Flowers

Agricultural Food and Environmental Chemistry
University of Glasgow, Glasgow G12 8QQ. Scotland

Keywords: adsorption, chromium, clean up technologies, bioremediation, leachates, waste water treatment.

Many organic waste materials are known for their ability to adsorb metals such as cadmium, chromium, copper, nickel, lead zinc, mercury etc. and this has been developed as means of cleaning up metal contaminated waste waters. In addition to providing a relatively low cost clean up method this also makes a positive use of what might otherwise be a waste material requiring disposal.

In the past this has been primarily concerned with the metal cations which in the case of chromium means the positively charged Cr^{3+} ion (oxidation state III). However, in the case of chromium, the soluble and mobile form in the environment is the Cr^{VI} oxidation state (the negatively charged dichromate or chromate ions). Hexavalent chromium is 100 to 1000 times more toxic than the common trivalent salts[1].

Work published in Europe and some trials carried out over the past few years in this department at Glasgow University have shown that some types of tree bark show a high affinity for the dichromate ion and that this could form the basis of a treatment system. It has been further shown that treatment of the bark can increase its ability to hold chromium. In one study ashing of dichromate treated bark showed that the ash contained up to 50% chromium.

Our studies show considerable variation in the affinities of barks from a range of tree species and other waste material for the two forms of chromium. Bark from coniferous trees such as Scots Pine were found to have a high affinity for chromate and dichromate while bark from deciduous species was found to have little ability to sorb Cr^{VI} but had a high affinity for Cr^{III}.

This adsorption could be utilised in 2 ways in low cost treatment/remediation schemes:

As a filter bed system for the removal of Cr^{VI} from an effluent stream.

As a soil ammendment on contaminated sites to reduce the solubility of chromium. This could have the benefit of reducing contamination in run off and leachate and, by reducing microbial and phytotoxicity, promote nutrient turnover and increased plant cover and therefore reduced dust hazard from the site.

Contaminated Soil '98, Thomas Telford, London, 1998, 925–926

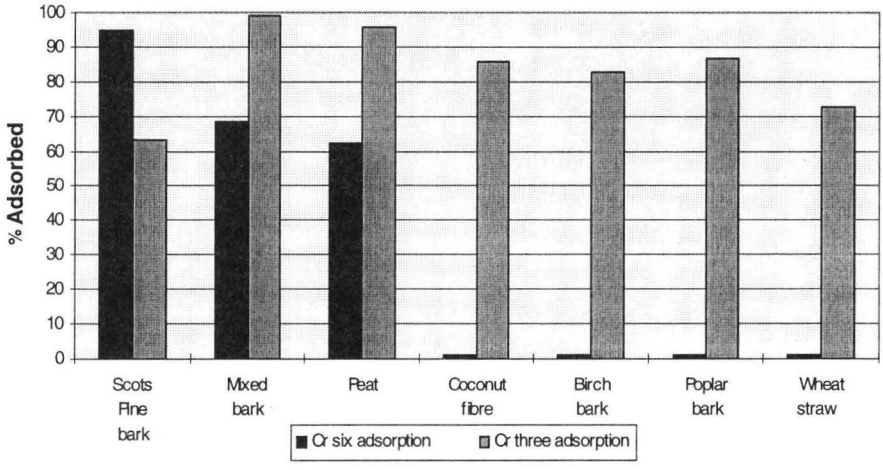


Figure1. Adsorption of Cr^{III} and Cr^{VI} by tree barks and organic waste materials

REFERENCES

1. Gauglhofer J and Bianchi V (1991) Chromium. In Metals and their compounds in the environment, edited by E Merian. VCH, Weinheim, Germany : 853-878.

2. Gaballah I, Goy D, Kilbertus G and Thauront J (1994) Decontamination of industrial effluents for environmental protection and recycling of metals. *Resouces, Conservation and Recycling 10, 97-106.*

THE FATE OF HEAVY METALS IN MATERIALS USED FOR LAND RECLAMATION

M.A. Fairley[1], J.G. Farmer[1], J.E. Paterson[2], S.J.T. Pollard[3] and R.M Rees[2]
[1]Environmental Chemistry Unit, Department of Chemistry, University of Edinburgh, Edinburgh, EH9 3JJ, Scotland
[2]Scottish Agricultural College, West Mains Road, Edinburgh, EH9 3JJ, Scotland
[3]National Centre for Risk Analysis and Options Appraisal, Environment Agency, Steel House, 11 Tothill Street, London, SW1H 9NF, UK

Key words: analytical methods, chemical speciation, fine particles, heavy metals, organic matter, mobility

Summary

Colliery spoil and sewage sludge may be used in the reclamation of contaminated land[1]. However, both materials contain heavy metals with a potential for release subsequent to application. When laboratory columns of spoil and sludge were irrigated, the resulting leachate contained zinc at >100 μg/l, barium at >250 μg/l and magnesium at >140 mg/l. Further analyses indicated that the transport of these metals was enhanced by the presence of fine particle sediment in the leachate.

Introduction

At the site of a former steelworks, Hallside, near Glasgow in Central Scotland, colliery spoil and sewage sludge have been employed during remediation. Colliery spoil provides a mineral framework for the development of an incipient 'soil' and the sewage sludge provides fertility and water-holding capacity through the addition of organic matter. However, both materials also contain heavy metals that could potentially leach from the site post-application. An assessment of the potential impact of metal leaching for such schemes[2] is required, within an overall context of land regeneration, in order to contribute to the long-term performance evaluation of remediation.

Method

Laboratory experiments were designed to test the hypothesis that heavy metals in the colliery spoil could potentially be mobilised through complexation with soluble organic molecules formed from the decomposition of sewage sludge[2]. PVC columns of colliery spoil and sewage sludge (at 300 t/ha), representing near field conditions, were irrigated with synthetic rain water for 70 weeks. Leachate was analysed for Zn, Cd, Pb, Ni, Cu, Ba, Mg, organic carbon and pH. The work also examined the physicochemical form of the metals: soluble (<0.45 μm, < 2.6 g/cm^3), adsorbed (0.2 M HNO_3) and residual (HNO_3/HCl). Additionally, a sequential extraction technique was devised to "speciate" the metals in the solid colliery spoil matrix.

Results and Discussion

1. Zinc, Ba and Mg concentrations (Table 1) were enhanced (~ x3) in the leachate from sewage sludge-treated columns relative to the untreated spoil controls.
2. Concurrent pH and DOC data inferred a correlation between metal concentration and pH, the lower pH corresponding to a higher metal concentration in the leachate. Although the sewage sludge mass in the columns decreased by 34%^{w}/w during the 70 week experiment, only 0.1%^{w}/w of this was found in the leachate. Thus it would appear likely that organic

matter loss may have influenced the mobility of metals indirectly, via a reduction in pH.

3. The concentrations of Ba (7 µg/l) and Mg (22 mg/l) leached from the sewage sludge alone were comparatively low. Enhancement of Ba and Mg can, therefore, be attributed to leaching from the colliery spoil, perhaps through displacement of cations by hydrogen ions produced during sludge decomposition. Although it is not possible to ascribe with certainty the source or mechanism of Zn release, as the sewage sludge itself contained Zn at 275 mg/kg (vs. 426 mg/kg for spoil), it is noteworthy that elevated Zn concentrations persisted for much longer in column leachate from sludge-treated spoil than from sludge alone.
4. Fractionation of the leachate indicated significant concentrations of Zn and Ba in the solution, adsorbed and residual forms (Table 1), while Mg was found predominantly in solution. Additionally, the presence of visible sediment influenced the relative proportions of metals between the solution and adsorbed forms. There was a marked decrease in the metals content of the solution phase and an increase in that in the adsorbed phase for samples with observable traces of fine sediment. The presence of fine sediment in the leachate was demonstrated to be an agent for the transport of metals in the experiments, noticeably reducing solution concentrations of Zn, highlighting the need to consider the adsorbed metal component during groundwater analysis.
5. The fractionation of colliery spoil indicated that no significant change occurred in the physicochemical form of Zn, Cd, Cu or Pb within the colliery spoil over the 70 week period. The metals were concentrated in the reducible (Mn/Fe oxyhydroxides - 30% of Zn) and the sulphide (55% of Zn) fractions.

Table 1: Comparison of Fractionated Column Leachate Concentrations (mean over 70 weeks and range 0-70 weeks) with UK Environmental Quality Standards (µg/l unless otherwise stated)

Metal	Dissolved	Adsorbed	Residual	Drinking Water	Inland Waters
Zn	51 (17-109)	17 (7-27)	28 (23-32)	100	8-500
Cd	<10			5	5[a]
Pb	<20			50	4-250[b]
Ni	<30			50	50-200[b]
Cu	<10			3000	1-28[b]
Ba	177 (61-259)	26 (2-50)	12 (5-26)	1000	n/a[c]
Mg[d]	92 (59-144)	6 (1-27)	0	50[d]	n/a

a: Annual average; b: Dissolved, hardness related; c: not available; d: mg/l

Conclusions

The ~3-fold enhancement of Zn, Ba and Mg concentrations in leachate from the colliery spoil when treated with sewage sludge under simulated field conditions demonstrates the need for assessment of the interactions and influence of reclamation materials upon contaminant mobility when considering remediation options for contaminated land.

References

[1] Wolstenholme, R.W. and Hall, J.E. (1996) Manual of Good Practice for the Use of Sewage Sludge in Land Reclamation, Water Research Centre, *in press*

[2] Fairley, M.A. *et al.* (1995) The Influence of Sewage Sludge Derived Organic Matter on the Mobility and Speciation of Heavy Metals in Colliery Spoil, *Proceedings 10th International Conference on Heavy Metals in the Environment*, CEP, Edinburgh, Volume 2, pp. 451-454

STABLE ISOTOPES AS TRACERS OF WATER FLOW AND GEOCHEMICAL INTERACTIONS RELATING TO LOW-LEVEL RADIOACTIVE WASTE DISPOSAL.

R.H.Walker[1], M.C.Graham[1], J.G.Farmer[1], A.E.Fallick[2], and D. Trivedi[3].

[1] Environmental Chemistry Unit, Department of Chemistry, The University of Edinburgh, Edinburgh, EH9 3JJ.
[2] Isotope Geosciences Unit, SURRC, East Kilbride, Glasgow, G75 OQF.
[3] BNFL, Risley, Warrington, Cheshire WA3 6AS.

KEYWORDS: groundwater monitoring, isotope hydrology, waste disposal sites.

INTRODUCTION

The aim of this project is to investigate the interactions between the groundwaters and stream waters at the Drigg low-level radioactive waste site in Cumbria. Hydrological and geochemical investigation have established a conceptual understanding of the site hydrology/hydrogeology. This study will use the investigation of stable isotopes to support and underpin the conceptual model, with respect to aspects such as the contribution of natural run off and groundwater to stream base flow. Previous geochemical investigations (e.g. major ion analyses, pH and conductivity measurements) of the stream waters and the groundwaters flowing through the site, have not been able to determine unequivocally the relative contributions from the different water sources, such as natural run-off and base flow.

The initial phase of the project has sought to determine if there is a statistically significant difference in the isotopic composition of the source waters. Individual meteoric waters (e.g. stream waters, groundwaters) can exhibit measurable differences in their $^{2}H/^{1}H$ and $^{18}O/^{16}O$ ratios (Gat, 1996). These variations are determined by the source of the water and any processes, such as evaporation, that the water body has undergone. In this study, water samples from three locations on the Drigg stream (which runs North-South) and two locations on the East West stream have been collected two-week intervals. In addition, runoff and borehole samples have been collected on a monthly basis from locations close to the streams, which are the two main surface water bodies traversing the site.

EXPERIMENTAL APPROACH

The stable isotope ratios ($^{2}H/^{1}H$ and $^{18}O/^{16}O$) in the water samples are reported as δ-values (δD, $\delta^{18}O$), in parts per thousand (‰) relative to V-SMOW, Vienna-Standard Mean Ocean Water. The hydrogen stable isotope analysis was performed using a dual inlet mass spectrometer, which measures the δ-value of the sample relative to that of a reference gas. $^{2}H/^{1}H$ ratio analysis was carried out on hydrogen gas produced by passing the water over a uranium furnace at 600°C (Friedman, 1953). The oxygen ratio was determined following equilibration of the sample with CO_2 gas (Roether, 1970). The pH and conductivity of the samples were measured on site following collection. Major ion analyses have been determined by ion chromatography and the concentrations of nitrate, sulphate and chloride utilised as 'markers' to distinguish between the different waters, or to demonstrate their connectivity.

Contaminated Soil '98, Thomas Telford, London, 1998, 929–930

RESULTS AND DISCUSSION

The samples analysed to date have δ-values ranging from –33‰ to -52 ‰ for δD, and from –5.7 ‰ to –6.9 ‰ for $\delta^{18}O$. A plot of δD against $\delta^{18}O$ for all of these samples can be fitted with a line of $\delta D = 8.26 \times \delta^{18}O + 10.6$, at a confidence level of 99%. This is in agreement with the Global Meteoric Water Line (GMWL) of $\delta D = 8.13 \times \delta^{18}O + 10.8$ (Rozanski, *et. al.*, 1993). When the δD vs. $\delta^{18}O$ plots were separated into the stream, runoff and borehole waters, it was observed that the borehole waters were more depleted in both D and ^{18}O than the stream waters (Figure 1). This suggests that the groundwaters and the stream waters may have different recharge areas/sources, or that the waters were recharged at different temperatures.

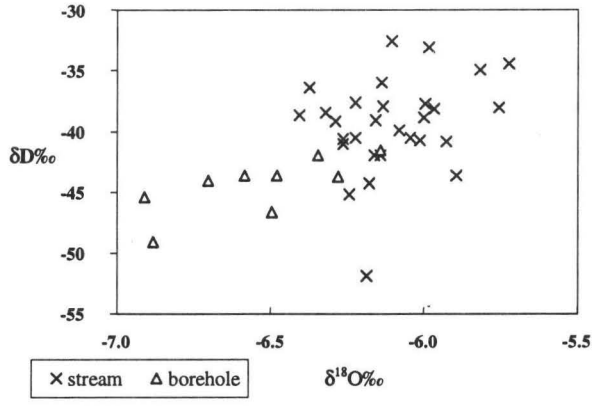


FIGURE 1
Plot of δD against $\delta^{18}O$ for the borehole and stream water samples from 26/3/97 to 4/6/97

Although difficulties relating to the complexity of the Drigg site have been encountered in the previous geochemical studies, the major ion analysis carried out in this study have revealed differences between the sample locations. For example, the sample locations on the East-West stream and those downstream of the confluence on the Drigg stream exhibit relatively high nitrate concentrations compared with upstream of the confluence on the Drigg stream. The differences between the borehole waters and stream samples are observed. The boreholes have lower concentrations of nitrate, sulphate and chloride than their neighbouring stream water sample locations.

CONCLUSION

The results from the initial three months sampling indicate that there are statistically significant differences in the isotopic signatures between borehole waters and surface waters. Borehole waters can also be distinguished from proximal surface waters on the basis of nitrate, sulphate and chloride concentration.

REFERENCES

Friedman, I., (1953) D contents on natural waters and other substances, *Geochim.Acta,* 4, 89-103

Gat, J.R., (1996) Oxygen and hydrogen isotopes in the hydrologic, cycle, *An. Rev. Earth Planet, Sci*, **24**, 225-262.

Roether, W., (1970) Water– CO_2 exchange set up for the routine assay of $\delta^{18}O$ of natural waters. *Int. J.Apl. Radiat. Isot.*, 21, 379-387

Rozanski, K., *et.al.* (1993) Isotopic patterns in modern global precipitation. *In: Continental Isotope Indicators of Climate*, American Geophysical Union Monograph.

THE INFLUENCE OF MICROBIAL ALTERATION OF HUMIC MACROMOLECULES ON HUMIC-ACTINIDE BINDING: IMPLICATIONS FOR ACTINIDE MOBILITY IN SOILS

S. I. Vinogradoff[1], A. Abbott[1], M. C. Graham[2] and J. G. Farmer[2]

[1]Westlakes Scientific Consulting Ltd, Westlakes Science & Technology Park, Moor Row, Cumbria CA24 3LN
[2]Department of Chemistry, The University of Edinburgh, King's Buildings, West Mains Rd, Edinburgh, EH9 3JJ
This work is funded by British Nuclear Fuels Plc.

Key words: Humic substances, isolation, microbiological degradation, radionuclides, soil.

Introduction

Organic matter, which makes up about 1-10% of the solid phase, plays many important roles (e.g. structure, water retention, cation exchange capacity) in soils. Humic substances are major constituents of the soil organic fraction but are an extremely complex, heterogeneous mixture of polyanionic macromolecules and their physical and chemical characteristics are not fully understood. It is, however, well known that they are important metal complexants and, for example, 50-100% of actinides: U, Pu and Np; may be bound to humic substances in soils (Scott *et al.*, 1991; Graham, 1993a).

Humic macromolecules are recalcitrant compounds with mean residence times in soil of the order of 100-1000 years (Stevenson, 1994). Microbiological degradation will, however, modify the functional group content (mainly COOH, OH) and hence the three-dimensional structure and orientation of the remaining functional groups of the humic molecules. Resultant changes in solubility and metal binding characteristics potentially have important consequences for actinide associations and mobility in soils. An objective of this project is, therefore, to investigate the microbial alteration of humic substances and the effect of this alteration on actinide binding capability.

Traditional procedures for the isolation of humic substances from soils involve: alkaline extraction; fractionation by acid precipitation of humic acids, leaving fulvic acids in solution and; purification (Stevenson, 1994). Criticism of these procedures has arisen due to the potential structural alteration under the harsh chemical conditions employed to obtain these extracts (Graham *et al.*, 1993b; Piccolo *et al.*, 1990).

This study has taken a new approach which involves "soft" biochemical methods in the extraction and fractionation of near-native humic macromolecules. The initial part of the work has, therefore, involved the development of a novel electrophoretic extraction procedure.

Methods

An accurately weighed amount of freeze-dried soil was mixed with a 50 mM Tris[1] buffer (pH 8.5) and the soil slurry applied to the electrophoresis well. A 1 % agarose solution was used to prepare the electrophoresis gel. The running buffer was a 45 mM Tris-borate solution, also at pH 8.5. Humic substances were electrophoretically extracted for 20 minutes at an applied voltage of 75 V. The pH of the aqueous solutions used in this study more closely simulate conditions found in natural systems than those used in traditional procedures.

Size separation of electrophoretic extractions was achieved by ultrafiltration using ultrafilters (Ultrafree-15, Millipore) of nominal molecular weight cut-off 5,000 D.

[1] Tris: Tris-(hydroxymethyl)methylamine

Results and Discussion

During the extraction, a brown band migrated from the well towards the anode (Figure 1). Following extraction, the gel was viewed under UV light and a second, previously undetected band, was observed immediately in front of the brown band (Figure 2).

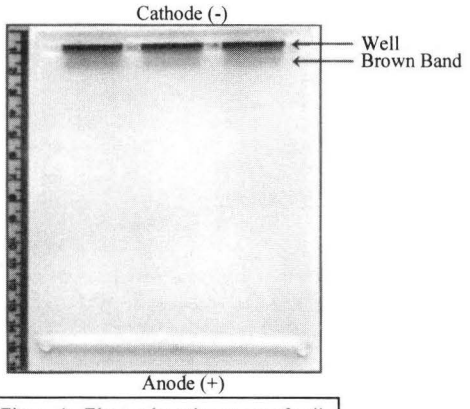


Figure 1: Electrophoretic extract of soil viewed in visible light. Soil slurry was applied to three wells and thus three adjacent brown bands are observed.

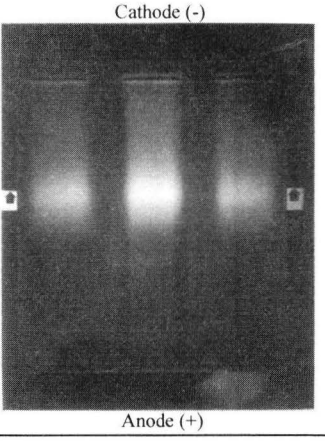


Figure 2: Electrophoretic extract of soil viewed in UV light. The soil slurry was added to three wells and thus three adjacent UV-fluorescent bands are seen. The arrows indicate the position of the front of the three brown bands.

The components of the UV-fluorescent band have potentially different chemical and physical characteristics from the those of the brown band since electrophoretic separation is achieved on the basis of differences in size, charge and shape of molecules. Further work, involving size fractionation of material from each of the two bands showed that the molecular size of components of the brown band was significantly greater than that of the UV-fluorescent band components. This is consistent with the greater electrophoretic mobility of the UV-fluorescent band. Further work (NMR, FTIR, electrospray mass spectrometry) is being undertaken to characterise more fully the components of the extracts.

Conclusions

A novel electrophoretic procedure for the isolation of humic substances from bulk soil has been developed and initial characterisation of the humic extracts has provided an estimate of molecular size. The extraction method is currently being applied in the investigation of microbial alteration of humic substances and isolation of humic components important for actinide binding in soils.

References

Graham, M. C., MacKenzie, A. B., Allan, R. L., Cook, G. T., Scott, R. D., Pulford, I. and Livens, F. R. (1993a) IR spectroscopy in the investigation of radionuclide binding in salt marsh sediments in SW Scotland, in R. J. Allan and J. O. Nriagu (eds) 9th International Conference Heavy Metals in the Environment Volume 2, CEP Consultants Ltd, pp 383-386.

Graham, M. C., Livens, F. R. and Scott, R. D. (1993b) Associations of actinides with soil humic substances in saltmarsh sediments in SW Scotland, in R. J. Allan and J. O. Nriagu (eds) 9th International Conference Heavy Metals in the Environment Volume 2, CEP Consultants Ltd, pp 243-246.

Perrin, D. D. and Dempsey, B. (1974) *Buffers for pH and Metal Ion Control*, Chapman and Hall, London.

Piccolo, A., Campanella, L. and Petronio, B. M. (1990) Carbon-13 Nuclear Magnetic Resonance spectra of soil humic substances extracted by different mechanisms, *Soil Science Society of America Journal, 54 (3), 750-756.*

Scott, R. D., MacKenzie, A. B., Ben-Shaban, Y. A., Hooker, P. J. and Houston, C. M. (1991) Uranium transport and retardation at the Needle's Eye natural analogue site, southwest Scotland, *Radiochimica Acta 52/53, 357-365.*

Stevenson, F. J. (1994). *Humus Chemistry: Genesis, Composition, Reactions, Second Edition*, John Wiley & Sons Inc.

Effect of temperature on toluene toxicity in psychrotrophic bacteria isolated or not from toluene polluted soil in a bioremediation perspective

A. Groboillot[1], G. Philippe[1], P.A. Chablain[2], N. Truffaut[2], J. F. Guespin-Michel[1]

(1) Laboratoire de Microbiologie du Froid, Université de Rouen, IUT de Biologie Appliquée, 43, rue Saint-Germain, 27000 Evreux, France and Université de Rouen, Faculté des Sciences, 76821 Mont-Saint-Aignan Cedex, France

(2) Laboratoire de Génétique Microbienne, Université de Technologie de Compiègne (UTC), BP 529, 60205 Compiègne, France

KEYWORDS: toluene, toxicity, bacteria, temperature, microbiological soil remediation

INTRODUCTION: Many environmental factors such as pollutant bioavailability and toxicity, temperature and pH affect the xenobiotic biodegradation in soil by inoculated microorganisms. The growth rate and the degradation rate in soil are dependent on the kinetic parameters of the inoculated strain which are largely influenced by these environmental factors and by their reciprocal interactions. In this study, two factors were investigated: temperature and xenobiotic toxicity.

Different psychrotrophic bacterial strains were considered for this study. Such cold adapted bacteria are of special interest for soil bioremediation in temperate climates. One of the tested bacteria able to degrade toluene (*Pseudomonas putida* 01G3) was a strain isolated from toluene polluted soil (Chablain *et al.*, 1997) and the other (*Pseudomonas fluorescens* MF37tol) was obtained by introducing Tol plasmid pWWO in the psychrotrophic strain *Pseudomonas fluorescens* MF37. This latter strain, corresponding to *Ps. fluorescens* MF0 rif^R was used as a control (Gügi *et al.*, 1991). Toluene was chosen as a model component. Although the effect of this toxic hydrocarbon on bacterial cell is well described in literature (Sikkema *et al.*, 1995), the effect of temperature on toluene toxicity was not studied yet. The toluene toxicity toward bacteria was tested as a function of temperature in various conditions: solid or liquid culture or in soil microcosm.

RESULTS: In all toxicity tests, bacteria were in presence of citrate and toluene. Citrate, inducing toluene catabolic repression, was first used by cells as carbon and energy source. The objective was to avoid toluene consumption in order to evaluate the pollutant toxicity.

For toxicity tests on solid medium, the exponentially grown bacteria were plated and toluene was dropped on a filter that was placed in the lid of a Petri dish. The percentage of surviving cells was plotted versus the toluene volume deposited on the filter, for the three strains, at 8°C and 28°C. The overall toluene toxicity toward all the strains is more important at 8°C than at 28°C. *Ps. putida* 01G3 demonstrated a higher toluene resistance than MF37 and MF37tol strains.

For toxicity tests in liquid medium, a culture of exponentially grown cells was aliquoted in tubes in which toluene was then added to reach a final concentration of 0.1% (v/v). Bacteria concentration was measured once in each tube, by successive dilutions and cell plate count. The concentration of surviving cells was determined as a function of time during 30 minutes following toluene addition. The slope of the semi-logarithmic scale curve was a reproducible measurement of toluene toxicity. For the three strains, toluene toxicity was determined at different temperatures (Fig. 1).

Toluene was more toxic at 8°C than at 28°C, but the toxicity showed a maximum around 17°C. *Ps. putida* 01G3 exhibited a lower resistance than the other strains.
For toxicity tests in soil microcosms, exponentially grown bacteria were added to the soil, in presence of toluene and citrate. The concentration of surviving bacteria was monitored. The results will be presented on the poster.

DISCUSSION AND CONCLUSION: The temperature effect on toluene toxicity could be attributed to the influence of temperature on toluene solubility. However, bacterial physiological properties cannot be excluded. Indeed, the temperature domain around 17°C, corresponding to the maximum toxicity, is also the critical temperature at which these bacterial strains exhibited in the Arrhenius plot a drastic change in slope (Chablain *et al.*, 1997). For *P. fluorescens* MF0, this critical temperature coincides with metabolic changes occurring at that temperature (Gügi *et al.*, 1991; Guillou and Guespin-Michel, 1996).
The discrepancy between the obtained results indicates the importance of the experimental conditions to evaluate toxicity. Increased toluene toxicity observed at low temperature has to be considered for bioremediation processes.

BIBLIOGRAPHY

Chablain P. A., G. Phillipe, A. Groboillot, N. Truffaut, J. F. Guespin-Michel (1997) Isolation of a soil psychrotrophic toluene-degrading *Pseudomonas* strain: influence of temperature on the growth characteristics on different substrates. *Res. Microbiol.* 148:153-161.

Guillou C. and J. F. Guespin-Michel (1996) Evidence for two domains of growth temperature for the psychrotrophic bacterium *Pseudomonas fluorescens* MF0. *Appl. Environ. Microbiol.* 62(9):3319-3324.

Gügi B., N. Orange, F. Hellio, J. F. Burini, C. Guillou, F. Leriche and J. F. Guespin-Michel (1991) Effect of growth temperature on several exported enzyme activities in the psychrotrophic bacterium *Pseudomonas fluorescens*. *J. Bacteriol.* 173(12):3814-3820.

Sikkema J., J. A. M. de Bont, B. Poolman (1995) Mechanisms of membrane toxicity of hydrocarbons. *Microbiol. Rev.* 59(2):201-222.

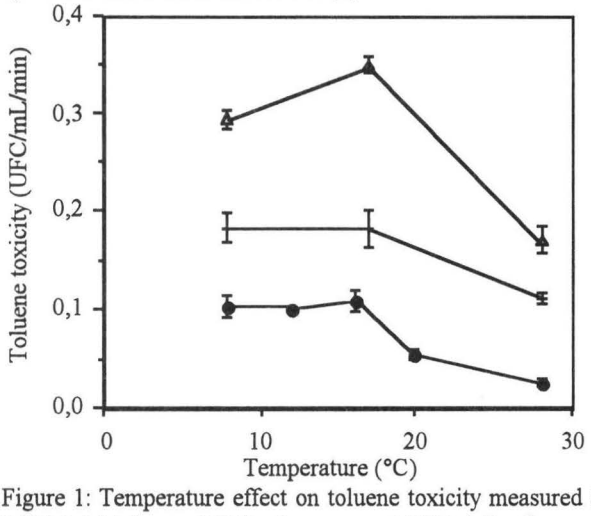


Figure 1: Temperature effect on toluene toxicity measured in liquid medium in the presence of 0.1% (v/v) toluene (● *Ps. fluorescens* MF37; + *Ps. fluorescens* MF37tol; ▲ *Ps. putida O1G3*)

IN-SITU BIOREMEDIATION OF POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs) IN GAS MANUFACTURING SITES; POSSIBLE ROLE OF INDIGENOUS AND AUGMENTED BACTERIA

ESMAEIL S. ALSALEH and JEREMY R. MASON

Division of Life Sciences, King's College London, Campden Hill Road, W8 7AH, U.K.

Key words: bacteria, biodegradation, characterisation, contaminated sites, ecotoxicological, *in situ* bioremediation, microorganisms, polynuclear aromatic hydrocarbons (PAH), remediation, sediments, soil, sorption

SUMMMARY

Polynuclear aromatic hydrocarbons (PAHs) degrading bacteria from soil samples were isolated on naphthalene as sole carbon source. Their substrate specificity and rate of PAH oxidation determined polarographically. One strain, EA100 was investigated further. The rate of ^{14}C naphthalene mineralization and the rate of disappearance of four PAHs in liquid culture was measured by high-pressure liquid chromatography. Having demonstrated the ability of this strain to degrade PAHs, it was employed for bioaugmentation studies in contaminated and pristine soil samples. Higher rates of ^{14}C naphthalene mineralization were detected for a pristine soil compared to that for contaminated soil. Bioaugmentation studies demonstrated that the low rates of PAH degradation in the contaminated soil were due to constrains and not to an inadequate indigenous microflora.

BACKGROUND

Polynuclear aromatic hydrocarbons (PAHs) constitute a group of priority pollutants which are present at high concentrations in the soils of many industrially contaminated sites, particularly those associated with the petroleum, gas production and wood-preserving industries. These compounds are of environmental and human health concern since some PAHs have been shown to be toxic, mutagenic, or carcinogenic (Gibson & Subramanian, 1984). Human exposure to PAHs may also occur from emissions during the incomplete combustion of fossil fuels or due to accidental discharge into aquatic and terrestrial environments during the transport, use, and disposal of petroleum products. There is therefore a clear need for method of remediation. The objective of *in situ* bioremediation is to use indigenous or introduced microorganisms to treat surface or subsurface contamination by providing direct contact between microorganisms and the free and sorbed contaminants in the soil (Madsen, 1991). The exploitation of microorganisms for the bioremediation of contaminated sites is a promising approach to pollutant clean-up. Bioaugmentation is one measure by which the degradation rate can be enhanced. A challenge for this approach is that, the introduced organism may not bring about the desired biodegradation after its addition to the soil (Goldstein *et al.*, 1985). In fact, both successes and failures have been reported when species capable of degrading the organic contaminants in culture were added to samples in natural environments. This failure could be due to physiological as well as ecotoxicological factors (Zaidi & Imam, 1996)

MATERIALS AND METHODS

Strains of bacteria capable of degradind PAH were isolated from sediment samples that were contaminated with PAHs from a gas manufacturing site. Using radiorespirometric based assay the ability of the indigenous flora and the augmented EA100 strain to mineralize PAH was estimated

RESULTS AND DISCUSSION

The isolated bacteria were able to degrade three and four ring PAHs in liquid culture at 30^{o}C. On the other hand,the rate of PAH degradation was seven fold higher in the pristine soil (9.5 ng/min/g soil) than that in the contaminated soil (1.3 ng/min/g soil) (Fig.1).

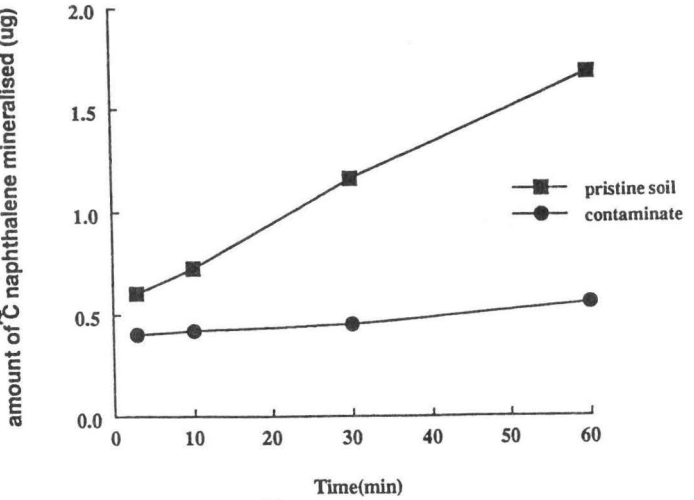


Fig. 1. Mineralization of ^{14}C naphthalene (0.5mmol/g soil) by the indigenous flora of contaminated (●) and pristine (■) soils (2 g) at 30 ^{0}C. Values are the average of two determinations, error bars lie within symbols.

Inoculation of soil with strain EA100 (1.35×10^9 cells/g soil) increased mineralization rates in both the contaminated and pristine soils (11.3 ng/min/g soil & 87.8 ng/min/g soil respectively) (Fig. 2).

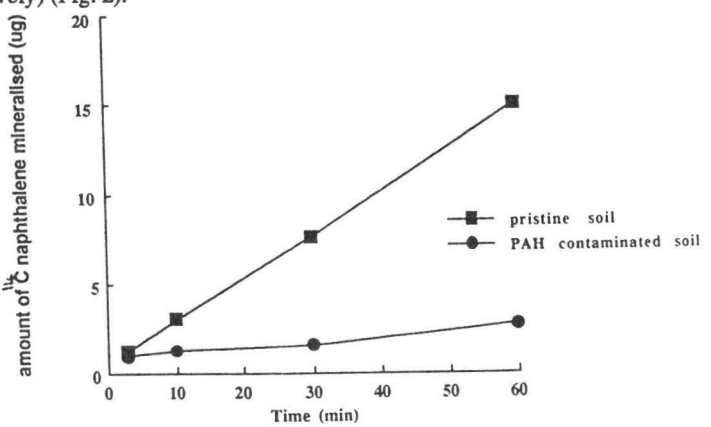


Fig. 2. Mineralization of ^{14}C naphthalene (0.5mmol/g soil)by bioaugmented EA100 (1.35 x 10^9cell/g) in contaminated (●)and pristine (■) soils (2 g) at 30 ^{0}C. Values are the average of two determinations, error bars lie within symbols.

REFERENCES

Gibson, D. T. & Subramanian, V. (1984). Microbial degradation of aromatic hydrocarbons. In *Microbial degradation of organic compounds*, pp. 181-242. Editted by D. T. Gibson. New York: Marcell Dekker

Goldstein, R. M., Mallory, L. M. & Alexander, M. (1985). Reasons for possible failure of inoculation to enhance biodegradation. *Appl Environ Microbiol* **50**, 977-983.

Madsen, E. L. (1991). Determining *in situ* biodegradation. Facts and challenges. *Environ Sci Technol* **25**, 1663-1673.

Zaidi B. R. & Imam, S. H. (1996). Inoculation to enhance biodegradation of phenolic compounds in industrial wastewater: isolation and identification of three-indigenous bacterial strains. *J Gen Microbiol* **42**, 249-256.

ACKNOWLEDGEMENTS

This work is supported by a grant from Kuwait government

GEOCHEMICAL SIGNATURES OF SELECTED HEAVY METALS IN CONTAMINATED SOILS, STREAM SEDIMENTS AND ALLUVIUM ASSOCIATED TO ONE CASE STUDY OF MINING EXPLOITATION IN PORTUGAL

J.M. Santos Oliveira[1] and Paula F. Ávila[1]
[1]Instituto Geológico e Mineiro, 4465 S. Mamede de Infesta, Portugal
Key words: Mine tailings, heavy metals, site investigation, sulphides, drainage

The present study concerns an investigation of the geochemical environment surrounding a recently abandoned but long established gold mine, the Jales Mine, located in northern Portugal. The ores extracted comprised a polymetallic gold-sulphide assemblage dominated by pyrite, arsenopyrite and various base metal sulphides and sulphosalts. During its lifetime the mine produced about 5 mt of fine-grained tailings (more than 60% less than 80 mesh) which were deposited in an open pit. Nearby the land is used for livestock rearing and crop cultivation.

To assess the environmental impact of toxic heavy metals, an extensive sampling survey of stream sediments, alluvium and soils was carried out around the mine, and the samples analysed for a suite of 21 minor and trace elements by Plasma Emission Spectroscopy with basis on a multielement strategy (Ávila and Santos Oliveira, 1997). Anomalous concentrations of the heavy metals As, Cd, Pb, Zn, Cu, Ag, W, Fe and Mn were detected, whilst other elements representative of the ores and the host rocks (e.g. Sb, Mo, Be, Ni and Co) were generally much lower or close to detection. Table1 compares the average concentrations for the most environmentally deleterious elements with baseline background values. The results clearly reveal strong contamination of the soils, stream sediments and alluvium by dispersal from the mine tailings.

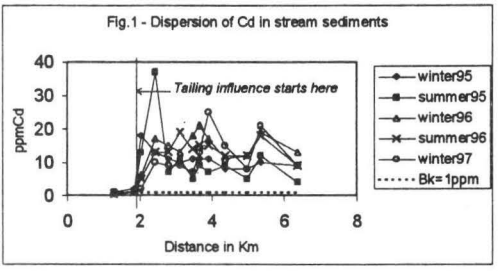
Samples	As	Cd	Pb	Zn	Cu	Fe(%)	Mn
Stream sediments(n=33)	502	5	166	191	22	2.1	501
Backg. stream sedim.(n=10)	12	1	50	57	16	1.3	290
Alluvium(n=45)	1368	7	685	376	168	5.1	784
Backg. alluvium(n=4)	56	<1	44	80	15	2.6	395
Soils(n=115)	227	1.2	110	124	28	3.2	313
Backg. soils(n=10)	29	<1	63	86	21	1.9	427
Mine tailings(n=18)	2960	29	810	1150	67	2.0	434
Granitic rocks(n=10)	10	<1	38	50	5	1.5	221

Table 1- Average element contents of As, Cd, Pb, Zn, Cu, Fe and Mn in stream sediments, alluvium, soils, tailings and rocks around the Jales Mine (values in ppm unless stated)

Statistical-mathematical treatment of the data using univariate and multivariate techniques shows that 80% of the total variance can be explained by two factors. The first factor indicates a strong association between As, Cd and Zn whilst the second shows the association between Cu and Pb with the Fe-Mn pair; the latter presumably as a consequence of secondary oxide and hydroxide formation. Using selective leaching techniques on stream sediment samples (Cardoso Fonseca, 1982) at least 63% of the total amounts of As, Cd, Cu, Pb and Zn are in mobile mineralogical sites (i.e. cation exchange, carbonates, amorphous Mn-Fe oxides and hydroxides).

Anomalous patterns of As, Cd, Zn and Pb could be found in the stream sediments 14 to 20Km downstream from the polluting sources. In detail it was shown that the highest geochemical contrasts were due to the finest grain size fractions (<200 mesh). Confirmation of the dispersal trends were proven by element maps and selected factor score maps derived from factor analysis. Biannual sampling over a 2 year period (1995-

97) demonstrated continuous mechanical and chemical erosion of the tailings, especially during the winter months when wet and windy conditions prevail (figure1 shows the example of the Cd distribution in stream sediments downstream from the mine site).



Concentrations of Cu, Fe and Mn are particularly elevated (as well as of As, Cd and Pb) in alluvium several hundred metres from the tailings site. Furthermore, their behaviour in the alluvium is in marked contrast to the stream sediments. They appear to be strongly fixed in the matrix and protected from further leaching. Such anomalous patterns have been developed over time and can be detected at depths of at least 40cm below the present surface. Many of the alluvium values are higher than critical levels proposed for contaminated soils (Thornton, 1983; Alloway, 1993; Ross, 1994).

In soils up to about 1Km around the tailings site, anomalous geochemical aureoles are found for As, Pb and Zn, and to a lesser extent Cd. These values are greatly attributed to wind blown the fine particulate material being removed from the dumps and scattered over the surrounding land. Without doubt, the main source of heavy metal contamination of the environment in the Jales area are the exposed mine tailings which are continually being dispersed into the stream sediments, alluvium and soils by mechanical and chemical erosion. Evidence exists that the situation is likely to worsen. The principal *risk factors* are:

- high concentrations of the heavy metals in the finest grain size fractions of the stream sediments
- persistence of significant concentrations of heavy metals throughout the alluvium sediment profiles
- association of heavy metals with low stability mineral phases
- predominance of very fine grain size fractions in the tailings
- existence of a well-developed drainage system and heavy rainfall during the winter promoting erosion, leaching and dispersal of the tailings.

To conclude, mining activities at the Jales Mine (up to 1993) have created a significant environmental risk to the surrounding area.

REFERENCES

-Alloway, R. (1993). *Heavy Metals in Soils*. Edited by B.J. Alloway. Blackie USA and Canada, Halsted Press, 339 pp.

-Ávila, P. and Santos Oliveira, J.M. (1997). Geochemical patterns of As, Cd, Pb, Zn and Cu in stream sediments and soils from a mining site in terms of an environmental impact assessment. *18th International Geochemical Exploration Symposium Abstracts, Jerusalem, pp.1-2.*

-Cardoso Fonseca, E. (1982). Emploi de l'extraction chimique sélective séquentielle et détermination des phases-support du Pb et du Zn en millieu silico-alumineux lors l'altération supergéne: exemple du prospect de Sanguinheiro (SE Aveiro, Portugal). *Comunic. Serv. Geolog. Portugal, t. 68, fasc. 2, pp. 267-283.*

-Ross, S.M. (1994).*Toxic Metals in Soil-Plant Systems*. Edited by Sheila Ross. John Wiley & Sons, Chichester, 469 pp.

-Thornton, I. (1983). *Applied Environmental Geochemistry*. Edited by Ian Thornton. Academic Press, London, 501 pp.

Uptake of 2,4,6-trinitrotoluene in herbaceous plants

P. Scheidemann, C. Sens and D. Werner

Department of Biology, Philipps-University of Marburg, Karl-von-Frisch-Str., 35032 Marburg
e-mail: scheidem@mailer.uni-marburg.de

Key words: plants, trinitrotoluene, phytoremediation, sequential extraction procedure

Summary
Herbaceous plants are able to take up TNT from soil or hydroculture. The concentration of nitroaromatic compounds (NAC) in the plant is dependent on the plant species and the TNT contamination level in the soils. Most of the NAC in the plant were found in roots, where they were equally distributed between the cytoplasmic and cell wall derived fractions.

Zusammenfassung
Untersucht wurde die Aufnahme von TNT aus dem Boden bzw. einer Nährlösung in krautige Pflanzen. Die Konzentration der Nitroaromaten (NAC) ist abhängig von der Pflanzenart und der TNT-Konzentration im Boden. Der größte Teil der aufgenommenen Nitroaromaten wurde in der Wurzel nachgewiesen, davon etwa 50 % in cytoplasmatischen Fraktionen, die andere Hälfte in Zellwandfraktionen.

Résumé
Les plantes herbacées sont capables d'ingérer le TNT du sol ou d'une solution nutritive. La concentration de composés nitroaromatiques (NAC) dans la plante dépend de l'espèce de la plante et du niveau de contamination en TNT dans les sols. La plupart des NAC ingérés furent décelés dans les racines, dont 50 % dans les fractions cytoplasmiques et 50 % dans les fractions des parois cellulaires.

For uptake studies in the soil/plant system eleven plant species (five dicotyledonous, six monocotyledonous species) were cultivated for eight weeks in standard soil under identical conditions in the greenhouse. The soil was contaminated with 10, 100 or 500 mg TNT/kg, respectively.
Plant roots were extracted using dichloromethane with acid hydrolysis followed by alkalinisation. The main TNT-metabolites measured by GC-ECD were 2-aminodinitrotoluene and 4-aminodinitrotoluene. There was a positive correlation between soil contamination and the concentrations of extractable nitroaromatic compounds (NAC) in the roots.
A species-dependent contamination level of extractable nitroaromatics was shown. The roots of *Triticum aestivum* and *Phaseolus vulgaris* grown in soil supplemented with 100 mg TNT/kg contained high levels of TNT-metabolites (98 µg NAC/g d. wt. and 91 µg NAC/g d. wt., respectively). In the same soil the lowest level of nitroaromatics was detected in the root extract of *Lupinus angustifolius* (14 µg/g d. wt.). General differences due to the diverse biochemical composition of monocotyledonous and dicotyledonous plants were not observed.

Contaminated Soil '98, Thomas Telford, London, 1998, 939–940

^{14}C-TNT was used to quantify the uptake rate of TNT into *Phaseolus vulgaris* and *Triticum aestivum* grown in hydroculture. Plants were analysed by a special fractionation method with polar and nonpolar solvents and enzymes. Three cytoplasmic fractions and five cell wall derived fractions were obtained. The recovery rate was 72 % in the case of bushbean and 101 % in the case of wheat by combustion and liquid scintillation counting. ^{14}C in both plant species partitioned into almost equal amounts with approximately 50 % in the cytoplasm and 50 % in the cell wall.
Most of the radioactivity in the cell wall was found in the lignin fraction. Investigations by thin layer chromatography refer to covalent linkages of TNT-metabolites with lignin. Nitroaromatic compounds of TNT in the cell wall are bound resulting in a probable long term immobilisation. The majority of TNT-metabolites in the cytoplasm in both plant species have an polar character and are not identified. They are under investigation by MS.

References

Cataldo D. A., Harvey S. D., Fellows R. J., Bean R. M. and McVeety B. D. (1989) An evaluation of the environmental fate and behaviour of munitions material (TNT, RDX) in soil and plant systems. Pacific Northwest Laboratories, Richland, *Report AD-A223 546.*

Görge E., Brandt S. and Werner D.(1994) Uptake and metabolism of 2,4,6-trinitrotoluene in higher plants. *Environ. Sci. & Pollut. Res. 4, 229-233.*

Görge E., Brandt S. and Werner D. (1995) Aufnahme von 2,4,6-Trinitrotoluol in Pflanzen. *UWSF - Z. Umweltchem. Ökotox. 7, 139-148.*

Klunk A., Görge E. and Werner D. (1996) Abreicherung von 2,4,6-Trinitrotoluol in Rizosphärenböden. *UWSF - Z. Umweltchem. Ökotox. 8, 243-247.*

Scheidemann P., Klunk A., Sens C. and Werner D. (1998) Species dependent uptake and tolerance of nitroaromatic compounds by higher plants. *J. Plant Physiol.* (in press).

DEVELOPMENT OF GEOCHEMICAL METHODS FOR THE DEGRADATION OF CHLORINATED ORGANIC CONTAMINANTS IN SEDIMENTS - LABORATORY SCALE (PART I)

Theofanis Zoumis, Wolfgang Calmano, Ulrich Förstner

Dept. of Environmental Science and Technology, Technical University of Hamburg-Harburg, Eissendorfer Str.40, D-21073 Hamburg, Germany

Key Words: barriers, chlorinated hydrocarbons, degradation, immobilization, organic contaminants, pesticide transport, sediments

INTRODUCTION

The Mulde river (Saxony, Germany) is, because of its extremely high contamination with heavy metals and organic pollutants, an enormous risk for the environment. In the Mulde area there are many abandoned open pits which can be used as sediment traps for contaminants bound on suspended matter. The pits have to be flooded with groundwater and a part of the river can flow through after that. One of these open pits is already used as a reservoir. Other researchers [1] made a GC-MS screening of the Mulde sediment earlier, and identified high concentrations of chlorinated organic contaminants, e.g. chlorobenzenes, DDTs and HCHs. There is always the danger of flooding and bioturbation which consequently leads to remobilization of pollutants. With the help of additives geochemical barriers are going to be built at the sediment / water interface which will have the purpose to immobilize the contaminants.

In this study, it should be demonstrated that modified or artificial created barriers are an effective, ecologically harmless and economic alternative to a treatment plant for the retention and elimination of contaminants.

THEORY

The spreading of organic pollutants can be prevented by geochemical barriers. These barriers have the purpose to adsorb or to precipitate dissolved contaminants and to enhance their availability to microorganisms and consequently their degradation.

Most studies in the last decades dealed with the dominating process in degradation of chlorinated hydrocarbons, the *reductive dechlorination*. Many investigations concentrated on methanogenic conditions, only a few were focused on sulphate-reducing conditions.

The degradation of chlorinated aromatics (e.g. hexachlorobenzene) in anaerobic environment takes place by gradually dechlorination, i.e. at every step a chlorine atom is replaced by a hydrogen atom (see Fig.1, Fig.2). The final compound of anaerobic degradation is dichlorobenzene. It is persistent in anaerobic sediment, but is degradable by aerobic organisms.

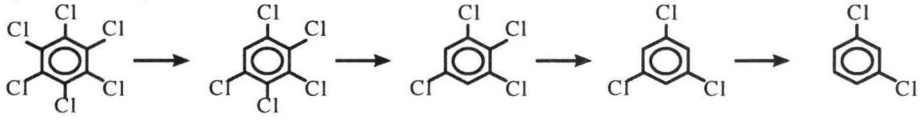


Figure 1: Degradation of hexachlorobenzene in sulphate-reducing environment [2]

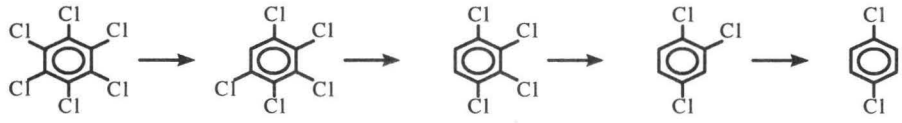


Figure 2: Degradation of hexachlorobenzene in methanogenic environment [2]

RESULTS AND DISCUSSION

The objective of this study is the development of natural in-situ treatment of contaminated sediments. For this reason the following questions have to be answered by the researchers:

* How are transport and degradation of organic contaminants in anoxic and sulphidic environment?
* Is there any positive influence of barriers (Fe, CO_3^{2-}, S^{2-}) on the immobilization of contaminants?

To investigate these tasks, an apparatus in laboratory scale was constructed (Fig. 3).

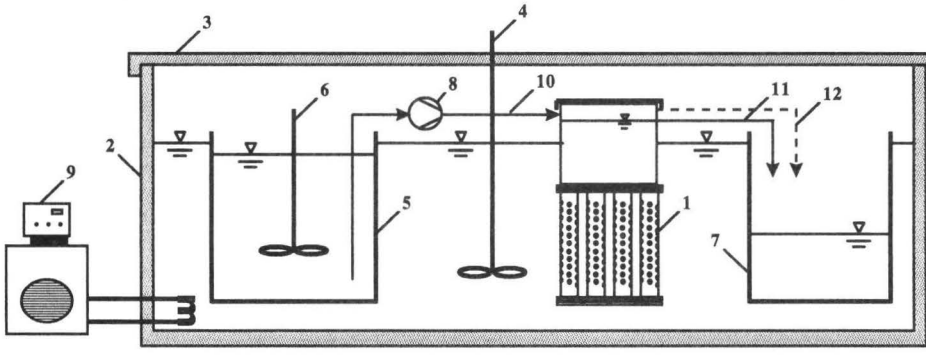


Figure 3: Laboratory apparatus for the investigations on the fate of organic contaminants in sediment cores (1:sediment cores with sampling points, 2: water bath, 3: water bath cover, 4: agitator temperature bath, 5: tank with Mulde river water, 6: agitator , 7: collecting tank, 8: pump, 9: thermostat, 10: inflow, 11: outflow, 12: overflow)

First results on behaviour and fate of chlorobenzenes and DDTs showed a slight difference to other studies [2] in degradation of HCB. The main degradation path starts with HCB and ends with 1,2 - DCB and 1,4 - DCB. DDT occurs mainly in the p,p configuration and is degraded to p,p -DDD and p,p - DDE.

REFERENCES

[1] Franke, S. et al. (1995): Identifizierung und quantitative Bestimmung organischer Substanzen in Wasser und Sedimenten der Elbe und der Mulde, *GKSS-Workshop, 177-189*

[2] Susarla, S., Yonezawa, Y.and Masunaga, S. (1997) Transformation kinetics and pathways of Chlorophenols and Hexachlorobenzene in fresh water lake sediments under anaerobic conditions, *Environmental Technology 18, 903-911*

RISK ASSESSMENT METHODOLOGY FOR SMALL / MEDIUM SCALE GROUNDWATER CONTAMINATION

Kenneth A. MacDougall[1] and George Fleming[2]

[1] University of Strathclyde, Glasgow, UK
[2] EnviroCentre Ltd / University of Strathclyde, Glasgow, UK

Keywords:

computer simulations; groundwater modelling: risk assessment: waste disposal sites

1. Introduction

A methodology is outlined which is suitable for use in assessing risks associated with sites where small to medium scale groundwater contamination may be present. Often when large scale contamination is known to have occurred then a detailed assessment will most likely be undertaken from the outset. However, the initial stages of this methodology may still prove useful as an initial screening tool.

A simplified approach is adopted which utilises a staged assessment strategy. The key features of the assessment include the creation of a database of known site parameters, use of simple groundwater flow models and application of a receptor based risk module.

2. Risk Assessment and Groundwater Contamination

The definition of risk assessment used for the purposes of this approach is:

analysing the potential for inflicting damage upon a receptor.

The recognised Source-Pathway-Receptor concept is adopted as the basis for the risk assessment. The source is generally recognised in cases of contaminated land or landfill sites. The pathway often holds the greatest degree of uncertainty, due to the lack of available data. However, the definition of the receptor may prove an issue for debate. Approaches vary from adopting the groundwater at the site in particular aquifers as being the receptor (Turrell et al., 1996), to the health of humans (ASTM, 1995) being the receptor. The receptor should be defined as being site specific and the risk assessment based on all receptors, with most vulnerable receptor representing the critical scenario.

3. Staged Risk Assessment

The staged strategy consists of primary, secondary and tertiary assessments. Each progression in the assessment requires an increase in modelling effort, analysis time, data requirements and financial resources.

The assessment may be undertaken as being receptor specific or source specific. For example, in the case of a landfill site with humans as the receptor at risk, the model

period may be either the receptor lifetime (70 years) or the source lifetime (~200-300 years).

4. Model Development

The initial assessment involves the development of a database which results in the production of a simple screening risk matrix, providing a qualitative analysis of the site. This allows the areas of concern and the most sensitive receptor type to be identified.

The subsequent assessments aim to further quantify the increase in risk to particular receptors. They utilise simple computer models whose complexity increases in relation to the extent of assessment required.

These assessment models comprise of groundwater flow models, the output of which is input to a risk module. Attenuation of contaminants is taken into account in these models, but again this depends on the degree of assessment required. The results of this analysis are an indication as to what extent the contamination is likely to increase the background risk to a particular receptor.

5. Case Studies

Two case studies are examined, both of which are landfill sites. They have been chosen due to several factors including the availability of historic and current data, the similarity of geological settings, and a variety of differing individual receptors.

6. Conclusions

Such a method may be undertaken for a landfill site with the database being continually updated as routine data collection occurs. This can allow assessments to be revised as and when necessary should any unexpected events occur. This will also allow the system to become increasingly tailored to a particular site and become an integral part of the site management.

7. References

ASTM (1995) *Standard guide for risk-based corrective action applied at petroleum release sites*, American Society for Testing and Materials, West Conshohocken, PA.

Turrell, J., Clark, L., Blackmore, J., Oakes, D., Buckland, J., Sims, P. and Wilkinson, M. (1996) *A Methodology to Derive Groundwater Clean-up Standards*, R&D Technical Report P12, Environment Agency, Bristol, UK.

DEVELOPMENT OF SAMPLING STRATEGIES FOR THE ASSESSMENT OF CONTAMINATED LAND

Dr. M.R. Harris[1] and Professor C. C. Ferguson[2]

1. Monitor Environmental Consultants Ltd, 400 Aldridge Road, Great Barr, Birmingham, B44 8BH, UK
2. CRBE, Nottingham Trent University, Burton Street, Nottingham, NG1 4BU, UK

Key words: Characterisation, sampling strategies, sampling programmes

BACKGROUND

Intrusive site investigation, and associated sampling and analysis, are important tools underpinning the whole process of assessing the human health and environmental risks that may be associated with contaminated land. Typically, site investigation costs account for a large proportion of the budget in any risk assessment project. It is essential, therefore, that site investigation generates data which are:

- adequate, given the objectives of the project
- relevant
- reliable, and
- clear

It is possible for the available information to be relevant, reliable and clear and yet still be inadequate for risk assessment purposes. For example, an important contamination source, pathway or receptor may have been missed, or its characteristics may have been poorly defined. Therefore it may be helpful to define the *minimum level of information* that should be collected for risk assessment purposes. Compliance with minimum information requirements should ensure significant omissions in the scope of the available data are avoided, and that a reasonable basis exists for decision-making. Data over and above this minimum level may be collected and, in general, will increase technical confidence in assessment findings. However, the extent to which additional data are collected will depend on a number of factors including:

- the balance between the cost (of carrying out the necessary work) and the improvement in technical confidence which may result from the work, bearing in mind the overall objectives of, and context for, the assessment;

- what is already known, or strongly suspected, about the site, and whether additional information is likely to change the assessor's view about its condition and any associated health and environmental effects;

- the consequences of failing to adequately characterise source-pathway-receptor relationships bearing in mind, for example, the nature, heterogeneity and likely

behaviour of the contamination source, the nature and predictability of the pathway, the nature and magnitude of possible adverse effects, and the "sensitivity" of the receptor;

- what options, other than more detailed data collection, may be available at any particular stage of the assessment.

It is important that the available information addresses all three components of a source-pathway-receptor relationship, and their respective characteristics. However, the variability of contaminant concentrations (at source, along a pathway, at the receptor or over time) may account for a significant level of technical uncertainty. Properly defining contaminant variability may also be expensive and time consuming.

DEVELOPING APPROPRIATE SAMPLING STRATEGIES

The poster describes a strategic approach to the development of sampling programmes that allows assessors to make explicit decisions about the balance between the costs (of assessment) and confidence in the outcome, while taking into account what other technical and non-technical options may be available.

A strategic approach to sampling should address such issues as:

- clearly defining both the context for, and objectives of, the assessment project;
- the nature of the priority receptors, sources and pathways and their role in determining sampling requirements;
- the degree of confidence that is required of (or can be attributed to) risk assessment findings as a function of the sampling regime.

It should also consider practical aspects, such as the need for integrated sampling that addresses different types of risk and classes of receptor and the phasing of site investigation works.

The poster gives particular emphasis to the specific sampling requirements associated with human health risk assessment, and the implications that spatial variation in contaminant concentrations may have for risk assessment findings. A statistical basis for comparing observed levels of contamination with generic or site specific assessment criteria relevant to human health is also discussed.

Acknowledgement

The poster is based on work being done as part of the research programmes on contaminated land managed by the UK Department of the Environment, Transport and the Regions (DETR) and the Environment Agency. The views expressed are those of the authors and not necessarily those of the DETR/Environment Agency.

THE SCOTTISH CONTAMINATED LAND FORUM: SOURCES OF INTERLABORATORY VARIABILITY IN THE ANALYSIS OF TOTAL METALS IN CONTAMINATED SOIL BY COMMERCIAL LABORATORIES

H J Duncan and T H Flowers

Agricultural, Food and Environmental Chemistry
University of Glasgow, Glasgow G12 8QQ. Scotland.

Keywords: analytical methods, metals, quality assurance, quality control

The Scottish Contaminated Land Forum has in the past 2 years set up an inter-laboratory testing group to examine the methods of routine analysis of heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn) in contaminated soils used by commercial laboratories. Three rounds have so far been completed. This has been used in part as a proficiency testing scheme by the laboratories but has also permitted an investigation of the sources of analytical variability within the 17 participating laboratories. This second aspect of the study is currently being developed and forms the main part of this presentation. The group has to a large extent overcome the concerns over commercial confidentiality and this has permitted a detailed investigation of the sources of variability between commercial analytical laboratories.

Overall levels of variability as shown by the % of satisfactory Z scores are comparable with those found in larger proficiency testing schemes such as the UK Contest scheme and many of the laboratories also participate in Contest.

For round 3 of the interlaboratory testing, 5 replicates of each of : a mixed (6 element) standard solution, a digest solution and a soil were circulated to each laboratory for analysis.

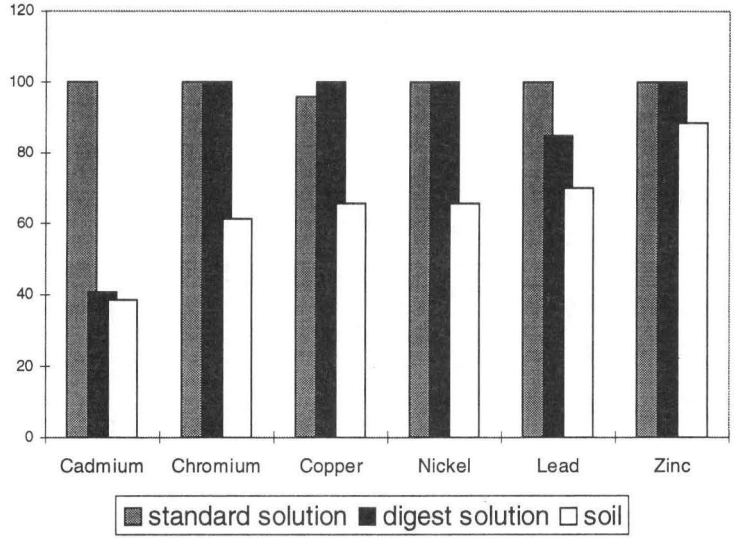


Figure 1. Percentage of Satisfactory Z Scores in Round 3

The results (see Fig 1) show a lower % of satisfactory Z scores for cadmium compared to the other metals. Three analytical methods were used within the group for the determination of cadmium:- flame atomic absorption spectrophotometry, graphite furnace atomic absorption spectrophotometry and inductively coupled plasma spectroscopy. The unsatisfactory high results were obtained by ICP-OES and this is attributed to the methods used for matrix interference correction in the different laboratories. When samples of the digests prepared by 14 laboratories were analysed by a single laboratory using AAS the RDS% was 15.9% compared to a RSD% of 134 % for analysis in the individual laboratories.

The other 5 metals all show the expected trend of an increase in variability with greater complexity of the analysis i.e. standard solution, < digest solution, < soil sample. Fig. 2 shows this trend for the analysis of copper. The level of variability in the analysis of standard solutions may be attributed to the quality control procedures used in the laboratories, commonly recalibration is carried out when check standards differ by more than 5% or 10%. The increase in variability for the prepared digest and for the soil samples suggests that the digestion step introduces a major component of inter-laboratory variability but that there is also an analytical component of interlaboratory variability.

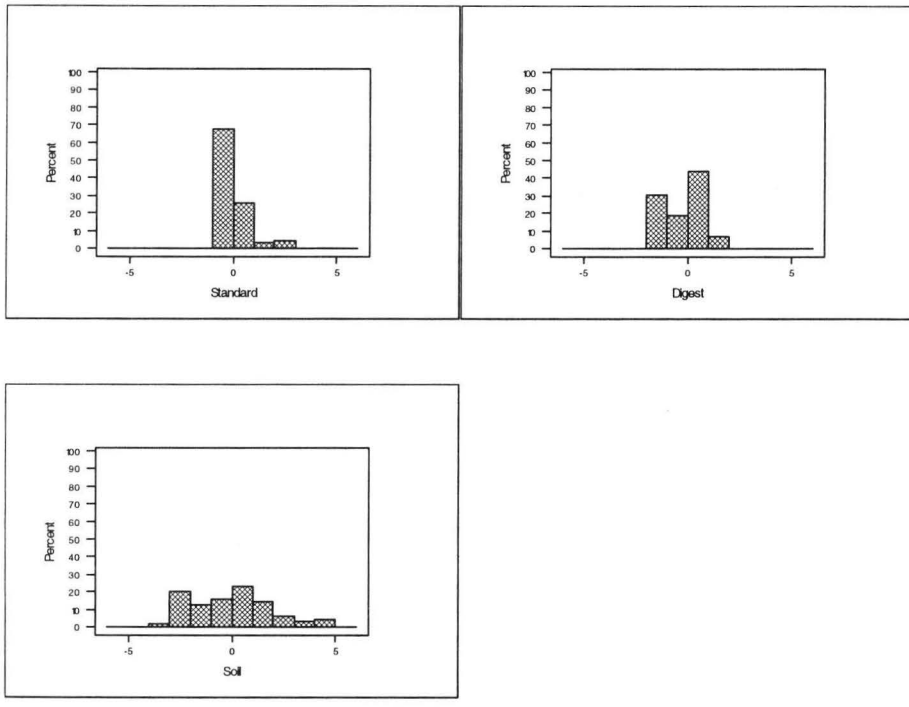


Figure 2. Distribution of Z scores for the Analysis of Copper in a Standard Solution, a Digest Solution and a Soil.

Kinetics of naphtalene biodegradation: determination of the kinetic and thermodynamic parameters

Elena Collina*, Giuseppina Bestetti#, Raffaella Ligorati*, Marina Lasagni*, Demetrio Pitea*

*Dipartimento di Chimica Fisica ed Elettrochimica, Università degli Studi di Milano via C. Golgi, 19 - 20133 Milano- Italy

#Dipartimento di Genetica e di Biologia dei Microorganismi, Università degli Studi di Milano - via Celoria, 26 - 20133 Milano

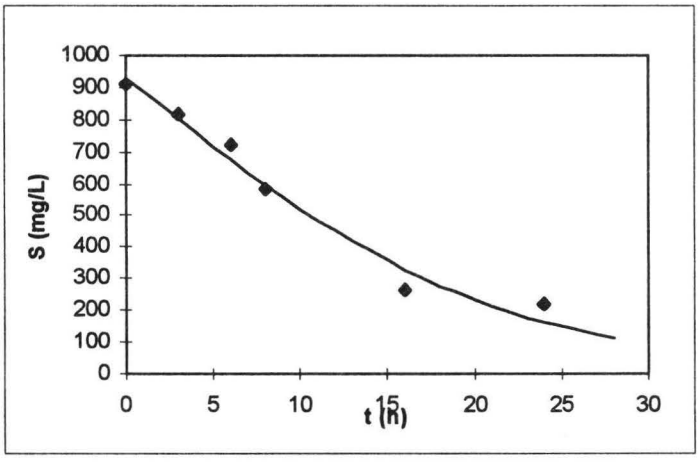
Keywords: naphtalene, biodegradation

Knowledge of the kinetics of biodegradation is essential to the evaluation of the persistence of organic pollutants, to forecasting the final contamination levels in a bioremediation process and to assessing exposure of humans, animals, and plants.
A 38000 m^2 contaminated area near Lodi, Italy, presented a diffuse naphtalene contamination.
From soil samples collected on the site, micro-organisms capable to degrade naphtalene have been selected.
Experiments on microbial degradation of naphtalene have been performed in flask at different temperatures, measuring at different times the population density and the residual napthalene.
An experimental procedure was set up for this purpose: population density was determined by measuring $\mathcal{D}$, absorbance of 540 nm wavelength radiation; residual napthalene concentration, S, was quantified with HPLC analysis after organic solvent extraction.
To fit the experimental data of both the naphtalene disappearance and the bacterial growth processes, a logistic kinetic model was used (Simkins, 1984):

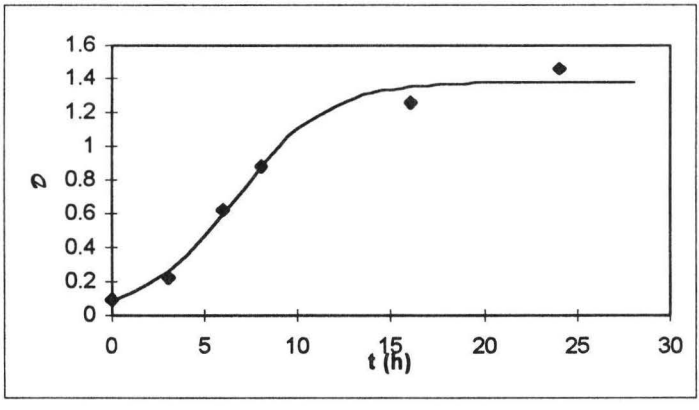
$$f(t) = \frac{b_0}{1 + b_1 \exp(b_2\, t)}$$

where the b_2 parameter has the dimensions of a first-order kinetic constant. At each experimental temperature (6, 23, 30, 37°C), the fitting was very good. As an example, in Figure 1 the experimental data at 23°C and the fitting curves are reported.
From the kinetic constant values, the activation and thermodynamic parameters for both processes were determined; their values are reported in the following table.

	Naphtalene disappearance	Bacterial growth
Activation parameters		
ln A	8.3 ± 0.8	21 ± 3
E_a (kJ mol^{-1})	26 ± 2	55 ± 8
Thermodynamic parameters		
$\Delta H^{\#}$ (kJ K^{-1} mol^{-1})	23 ± 2	53 ± 8
$\Delta S^{\#}$ (kJ mol^{-1})	- (0.252 ± 0.007)	- (0.14 ± 0.03)
$\Delta G^{\#}$ (kJ mol^{-1})	97 ± 2	94 ± 8



a) Naphtalene disappearance



b) Bacterial growth

Figure 1 - Experimental data at 23°C and fitting curves.

References:
Simkins, S. and Alexander, M. (1984), Models for mineralization kinetics with the variables of substrate concentration and population density, *Applied and Environmental Microbiology*, **47**, 1299-1306

Characterization of a contaminated site: Principal Component Analysis as a tool to rationalize data heterogeneity

Marina Lasagni, Elena Collina, Demetrio Pitea

Dipartimento di Chimica Fisica ed Elettrochimica, Università degli Studi di Milano via C. Golgi, 19 - 20133 Milano- Italy

Keywords: characterisation, data analysis

The study is part of a project funded by the Italian National Research Council for the development of a general strategy for the management and remediation of contaminated soils.

A 38000 m^2 contaminated area near Lodi, Italy, was chosen for experimental activity. Previously, a collection of information, witnesses and data available for activities reconstruction and a preliminary evaluation was performed.

From 1961 to 1986 five different industries have operated at the site. Their activities were: production of chemicals, such as phtalic anhydride; recovery of solvents; and handling and storage of exhaust oils. Possible contaminants deriving from these activities are: the chemicals themselves, residues from the production cycle, residues from solvent distillation, oil residues contained in six storage tanks still present. Moreover, after cease of the industrial activities, the site was used for illegal disposal of plastic bags containing tar residues (so-called "big bags") and burial of waste of unknown origin. Therefore, the sources of contamination can be numerous, and the pattern of contamination can be very complex.

In the past years, a large number of chemical analyses were performed on soil samples and samples collected in the oil tanks and from the big-bags, leading, in some cases, to very different results. To investigate sample homogeneity before final disposal, Principal Component Analysis, PCA, was used. PCA is a multivariate eigenvalue/eigenvector method designed to extract information in a data set. It reduces large numbers of variables to smaller ones which summarize the information and highlight the dominant patterns or major trends in the data. The new variables, called PC or principal components, are linear combinations of the original ones. For each component, the absolute value of the "loading" indicates how much the variable contributes to that PC. The "score" projection in the PC plane indicates the presence of grouping among objects.

PCA was performed on three data sets of autoscaled analytical results, where the samples represent the objects and the analytical parameters the variables:

1. Oil samples from the tanks, 7 objects × 15 variables;
2. Samples from big-bags, 5 objects × 20 variables;
3. Soil samples, 23 objects × 16 variables.

For data set 1, PC1 and PC2 sum up 73.9% of the information content of the data set. From the score projection in the PC1-PC2 plane (Figure 1) we may notice a group of three objects, namely the samples collected from the superior part of tanks 1, 2 and 3; the other objects are quite scattered. In fact, tanks 1 and 2 stored carter and hydraulic oil, tank 3 stored carter oil. Tank 6 stored industrial oil, the content of tanks 4 and 5 is unknown.

For data set 2, the first four PC sum up 100% of the original information. Sample homogeneity is confirmed.
For data set 3, PC1 and PC2 sum up 62.0% of the information content of the data set. From the score projection in the PC1-PC2 plane (Figure 2) we may notice the grouping of samples collected at the same depth. This result is related to the illegal burial of waste which determined the presence, at different depths, of materials of different density.

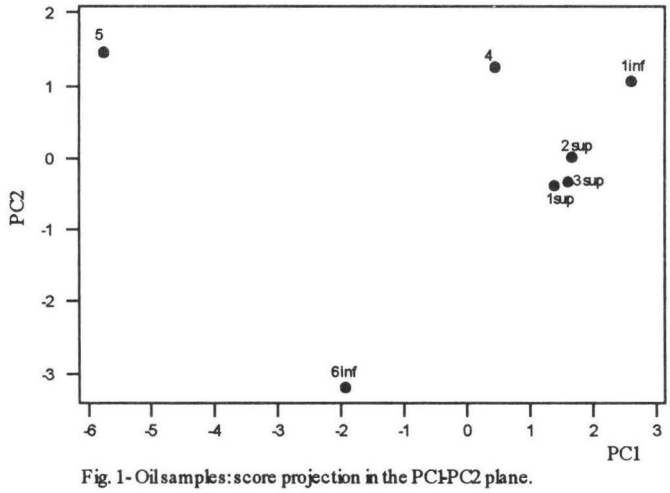


Fig. 1 - Oil samples: score projection in the PC1-PC2 plane.

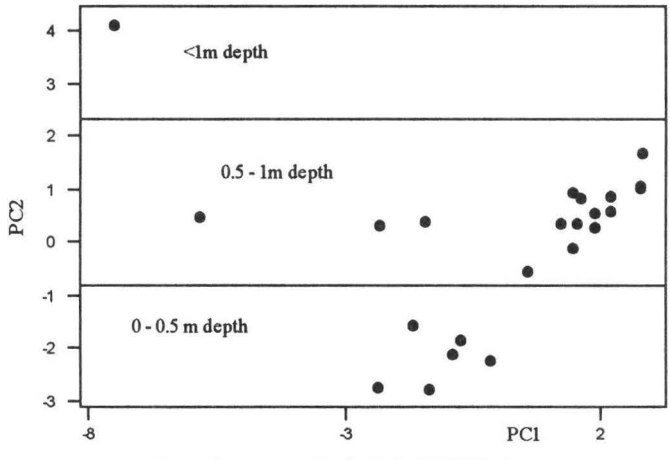


Fig. 2 - Soil samples: score projection in the PC1-PC2 plane.

The Effect of Organic Matter Composition on the Interaction between PAHs and Organic Sorbents in Soil

M. Schoone[1], M. W. I. Schmidt[2], I. Kögel-Knabner[2]

[1] Arbeitsgruppe Bodenkunde, Ruhr-Universität Bochum, 44780 Bochum, Germany,
[2] Lehrstuhl für Bodenkunde, Technische Universität München, 85350 Freising- Weihenstephan, Germany

Key words: Behaviour of contaminants, contaminated soil, distribution coefficients

Introduction

Soil organic matter (SOM) is the most important sorbent for hydrophobic organic chemicals (HOCs) e.g., polycylic aromatic hydrocarbons (PAHs) in soils (Karickhoff et al., 1979). A relationship between the content of soil organic carbon and the sorption behaviour of HOCs has been reported for sediments resulting in similar K_{OC} values for a specific hydrophobic organic compound. Recent investigations (Grathwohl, 1990; Rutherford et al., 1992; Kile et al., 1995), however, show different K_{OC} values for HOCs in soils and sediments suggesting that soil properties besides the organic carbon content influence the sorption behaviour of these chemicals. The chemical composition of SOM, such as aromaticity and polarity, is supposed to affect the sorption of HOCs. In the present study the influence of SOM composition on the sorption of pyrene and phenanthrene in natural soils and soils with anthropogenic organic matter is investigated.

Materials and Methods

Surface horizons of natural soils (Dystric Gleysol, Haplic Alisol, Haplic Podzol) and soils with anthropogenic organic sorbents from disperse atmospheric input such as brown coal and fly ashes (Urbic Anthrosols, Haplic Podzol, Haplic Phaeozem) have been investigated. In addition, studies have been carried out with organic materials such as brown coal and bituminous coal. Structural information about SOM was obtained by ^{13}C CPMAS NMR spectroscopy. Polarity of organic matter was calculated from the ratio (carboxylic C+O-alkyl-C)/(aromatic C+alkyl-C). Sorption experiments have been performed with ^{14}C-labelled pyrene and phenanthrene in batch experiments at room temperature using 1 mM $CaCl_2$-solution.

Results and Discussion

The natural soils, soils with anthropogenic organic matter and organic materials differ distinctly in organic carbon content and composition of the organic matrix.

As a consequence of the anthropogenic influence the soils with organic materials are high in organic carbon content (49-139 mg/g) in comparison to the soils from natural sites with 15-19 mg organic carbon mg/g.

SOM from soils with anthropogenic organic matter and the organic materials investigated exhibit higher signal intensities for aromatic carbon (25-79% of total signal intensity) compared to SOM from natural soils (17-25% of total signal intensity). SOM polarity is higher for natural soils (0.8-1.1) when compared to the other sorbents investigated in this work (0.1-0.6; Haplic Podzol, fly ashes: 1.2).

Sorption of pyrene and phenanthrene to soils and organic materials is influenced to a great extend by the organic carbon content (correlation coefficient r_s= 0.85 for pyrene;

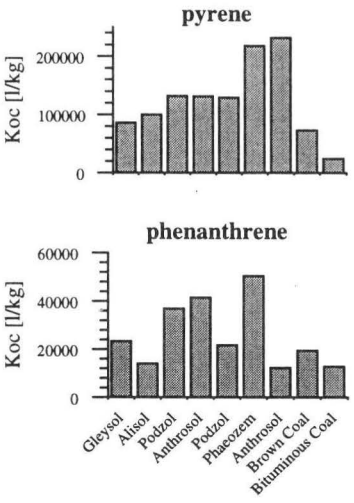


Figure 1: Distribution coefficients K_{OC} for pyrene and phenanthrene

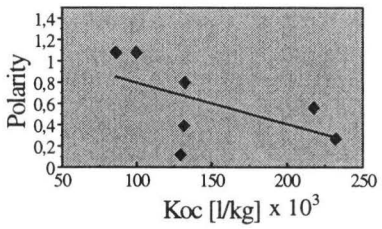


Figure 2: Correlation between polarity of organic matter and K_{OC} of pyrene to soils

0.90 for phenanthrene). Accordingly, the natural soils exhibit distinctly lower sorption capacities for the PAH compounds in comparison to the other sorbents.

Sorption capacities of organic matter for pyrene and phenanthrene show no relationship to chemical composition of the sorbing material when all sorbents are considered (Figure 1). However, considering soils only, the interaction between SOM and pyrene is indicated to be influenced by SOM polarity (r_s=-0.78; $p< 0.04$) (Figure 2). The lower polarity of SOM the higher is the sorption capacity for pyrene. Consequently, sorption of pyrene to SOM in the soils with anthropogenic organic matter (log Koc 5.11-5.37 l/kg) is higher compared to sorption to natural soils (4.93-5.12 l/kg). For phenanthrene no such effect has been observed.

SOM composition does not exhibit a uniform effect on the interaction between PAHs and organic sorbents in soil. The interaction between pyrene and SOM is suggested to be affected by the polarity of the organic matrix resulting in higher sorption capacities for less polar organic sorbents. The interaction between phenanthrene and the organic matrix, however, is not influenced by the composition of organic matter.

Acknowledgements:
The authors thank the EC (Environment and Climate Programme, EV-5V-CT94-0536) for supporting this work.

Literature

Grathwohl P. (1990): Influence of organic matter from soils and sediments from various origins on sorption of some chlorinated aliphatic hydrocarbons: Implications on K_{OC} correlations. Environ. Sci. Technol. 24, 1687-1693.

Karickhoff S. W., Brown D. S., Scott T. A. (1979): Sorption of hydrophobic pollutants on natural sediments. Water Research 13, 241-248.

Kile, D. E., Chiou C. T., Zhou H., Li, H., Xu, O. (1995): Partition of nonpolar organic pollutants from water to soil and sediment organic matters. Environ. Sci. Technol. 29, 1401-1406.

Rutherford D. W., Chiou C. T., Kile D. E. (1992): Influence of soil organic matter composition on the partition of organic compounds. Environ. Sci. Technol. 26, 336-340.

Pb Isotope Signatures: Evidence of Origin and Fluxes of Heavy Metals in an Area Polluted During 2000 Years of Pb-Zn Mining and Smelting

Renate Metzger[1], Ulrich Kramm[1], Jurian Hoogewerff[2] and Albrecht Baumann[3]

[1] RWTH Aachen, Institut für Mineralogie und Lagerstättenlehre, Wüllnerstr. 2, D-52056 Aachen
[2] Bundesversuchs- und Forschungsanstalt Arsenal, Faradaygasse 3, A-1031 Wien
[3] Universität Münster, Institut für Mineralogie, Corrensstr. 24, D-48149 Münster

keywords: contaminated soil, heavy metals, lead, isotope methods, mining, plants, behavior of contaminants, extraction, fixation

Pb isotope signatures are applied to identify the sources and pathways of lead in the Stolberg area, a highly contaminated Pb-Zn mining and smelting site in the Northern Eifel (Germany). Transport processes within soil profiles and from soils into plants are deduced from Pb isotope signatures and heavy metal concentrations.

Heavy metal pollution of up to 8000 ppm Pb, 2000 ppm Zn, 150 ppm As and 40 ppm Cd in upper A-levels of the soils is of both geogenic and anthropogenic origin. The geogenic source of lead is represented by the Pb-Zn mineralization of carbonate rocks. These ores have been mined and smelted in the Stolberg area from Roman times until 1919. Currently, imported lead ores are processed at the Stolberg smelter, which is the only primary lead smelter in Germany. Additional anthropogenic lead is derived from aerosols emitted from gasoline combustion, power plants, iron and steel manufacturing.

Several sources of lead in the upper soil levels are identified by their significantly different Pb isotope signatures. Lead in soils derived from recently processed Pb ores and from aerosol lead is isotopically distinguished from Stolberg Pb-Zn ores. Pollution by mining and smelting of local ores reflects the geogenic background. Authigenic soils from different parent rocks record the heavy metal pollution in different ways: Sandstone-derived soils show decreasing $^{206}Pb/^{207}Pb$ signatures from the source rocks towards the topsoils from 1.20 to 1.15-1.16 which is attributed to anthropogenic input. Limestone-derived soils, in contrast, are dominated by the local Pb isotope composition of $^{206}Pb/^{207}Pb = 1.18$ (Fig. 1). Pb isotope signatures of sandstone-derived soil profiles provide evidence of a recent migration of anthropogenic lead from topsoils down to a depth of at least 20 cm.

In order to determine the origin of the heavy metal pollution in the Stolberg area, several sources of heavy metals are identified by their Pb isotope signatures. Their contribution to the contamination is quantified using concentration data. The natural background is deduced from parent rocks of the soils and from pre-industrial lake sediments from the Eifel. The present-day long distant aerosol component is concluded from recent lake sediments and from dust sampling in the Eifel, i. e. outside of the immediate influence of the smelter emissions. Current immissions in the Stolberg region are monitored by dust sampling in the vicinity of the lead smelter.

Fluxes of heavy metals are considered by investigation of plants growing in the Stolberg area. Extraction tests help define the potential bioavailability of heavy metals. Plants show extremely high levels of heavy metal contamination close to the smelter. Mean soil-plant transfer increases in the order of Pb (0.5%) < Zn (17%) < Cu (23%) <

Cd (27%). Extraction tests with ammonium nitrate confirm these results and show reduced mobilisation of Pb and Cu caused by fixation to organic matter in upper A-levels. According to their Pb isotope signatures, the extractable fractions are concluded to be of anthropogenic origin.

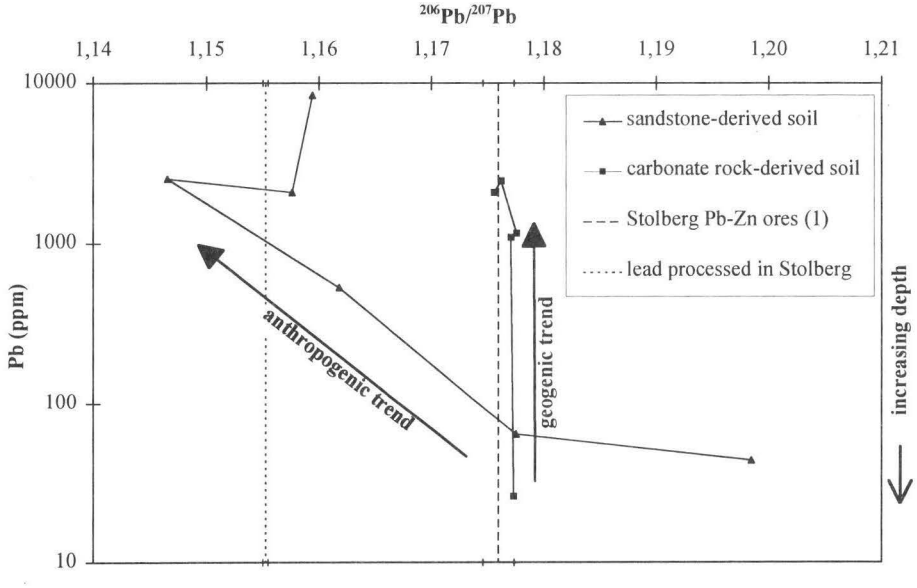


Fig. 1: $^{206}Pb/^{207}Pb$ signatures vs. Pb content of two soil profiles, the lowest point represents the parent rock. Geogenic Pb enrichment in the soil developed on a carbonate rock is distinct from anthropogenic input in the sandstone-derived soil.

References:

(1): Krahn, L. and Baumann, A. (1996) Lead isotope systematics of epigenetic lead-zinc mineralization in the western part of the Rheinisches Schiefergebirge, Germany, *Mineralium Deposita, 31, 225-237.*

The XUMA-GEFA Knowledge-based System for the Investigation and Evaluation of Contaminated Sites in Baden-Württemberg and Saxony

Wolfgang Ferse
Forschungszentrum Rossendorf, Postfach 510119, 01314 Dresden, Germany

Werner Geiger, Matthias Reißfelder, Rainer Weidemann
Forschungszentrum Karlsruhe, Postfach 3640, 76021 Karlsruhe, Germany

Thomas Reitz
Technische Universität Dresden, Fakultät Informatik, 01062 Dresden, Germany

Keywords: expert systems, risk assessment, site investigation

1. Introduction

The knowledge-based XUMA-GEFA system /1,2/ was developed to support the employees of authorities and engineering offices working in the field of contaminated site evaluation. The system provides the official with the technical knowledge required for the investigation and evaluation of contaminated sites and relieves him from routine work. Furthermore, it contributes to establishing a uniform procedure when dealing with the suspicious contaminated sites in the states of Baden-Württemberg and Saxony. The system was developed by the research centers of Karlsruhe and Rossendorf (FZK and FZR) and Dresden University in cooperation with the State Institute for Environmental Protection of Baden-Württemberg (LfU) and the State Authority for the Environment and Geology of Saxony (LfUG).

2. User Functions of the System

The system comprises various user functions for the investigation of contaminated sites. These are in particular:

- Evaluation of contaminated sites, e.g. determination of the hazard coefficient of suspicious dumps for specifying the actions needed and their priority during further investigation and remediation
- Preparation of analysis plans for the chemical and analytical investigation of suspicious sites.

The contaminated site evaluation function is based on the evaluation system applied in the state of Baden-Württemberg.

3. Generation of User Programs

The knowledge for the user functions is stored in a knowledge base. For the maintenance and management of the knowledge base by the experts, the system is equipped with a knowledge acquisition facility.

Due to the state-specific features, both states maintain and manage a knowledge base of their own at the central authority of the respective state (LfU in Baden-Württemberg, LfUG in Saxony). From time to time, the knowledge base is exported for the generation of execution systems on a PC. There, they are integrated in the user functions by means of a generation program. The user functions are supplied to the authorities and engineering offices of the states via a distributor on behalf of the respective state authority.

Low-cost implementation of the programs in both states in spite of the evaluation methods which were varying in detail was ensured by a multi-state concept for the evaluation function. It allowed to use the same knowledge acquisition facility (with a switch for the state-specific parts) in both states and to generate the state-specific user programs from a common source code.

4. Use of the System

The XUMA-GEFA evaluation program has been applied as the official program of the environmental protection ministries in the states of Saxony and Baden-Württemberg since the middle of 1996 and the beginning of 1997, respectively. The program is integrated in the entire contaminated site investigation procedure of these states /1,3/.

With the XUMA-GEFA system, the information cycle for contaminated site evaluation in the states of Baden-Württemberg and Saxony has been closed. The cycle can be adapted dynamically to the evaluation methods in the respective states without any further programming expenditure being required. By using such an approach of multi-authority, computer-aided contaminated site evaluation, these states fulfil a pilot function. Due to the described flexibility of the program system, even other states which employ a variant of the Baden-Württemberg evaluation procedure may use the XUMA-GEFA program system.

5. References

/1/ Ferse, W.; Geiger, W.; Reißfelder, M.; Reitz, T.; Schneider, U.; Weidemann, R.; "Das wissensbasierte System XUMA-GEFA für Altlasten: Vom Prototyp zum Produktionssystem"; Umweltinformatik '97; 11. Internationales Symposium der Gesellschaft für Informatik; Straßburg, 10. - 12. September 1997

/2/ Ferse, W.; Reitz, Th.; "Die Anwendung wissensbasierter Methoden bei der Bewertung von Altlasten"; XPS'97, 4. Deutsche Jahrestagung Wissensbasierte Systeme, Bad Honnef, März 1997

/3/ Ferse, W.; "A Computer System for Evaluation of Contaminated Sites"; Environmental Engineering and Pollution Prevention - European Network of Excellence and Partnership, NATO ASI Series 2: Environment - Vol. 18, Kluwer Academic Publishers, 1996

EVALUATION OF BIOREMEDIATION PROCESS EFFICIENCY : CONTRIBUTION OF ANALYTICAL, MICROBIOLOGICAL, MOLECULAR AND ECOTOXICOLOGICAL TESTS

V. Ducrocq[1], S. Hallier-Soulier[1], P. Pandard[2], E. Thybaud[2], N. Truffaut[1]

1- Laboratoire de Génétique Microbienne, Université de Technologie de Compiègne cedex, France. 2- Laboratoire d'Ecotoxicologie, INERIS, BP2, 60550 Verneuil-en-Halatte, France

Key words : bacteria, biodegradation, ecotoxicological tests, microcosms, PCB, remediation efficiency, toxic metabolites.

SUMMARY

The aim of this work is to underline the need to use various techniques in order to estimate the efficiency of a biodegradation process in polluted soils. Several techniques are proposed to follow the depollution mechanism : analytical techniques, microbiological and molecular methods and ecotoxicological tests. Quantitative PCR tools were constructed to detect two strains : a biphenyl degrader *Pseudomonas* sp. B4 and a 4-chlorobenzoate degrader *Pseudomonas* sp. CBS3. This technique is a powerful system to estimate a number of bacteria more reliable than enumeration with microbiological methods, particularly when cells are in a viable but non culturable state.

The disappearance of the initial pollutant (4-chlorobiphenyl) followed by analytical methods were not conclusive to establish whether the remediation was effective or not. The ecotoxicological tests showed that the lowering of the concentration of 4-chlorobiphenyl did not induce a detoxification of soil microcosms. Furthermore, the detoxification occurred only at a low amounts of intermediate metabolites, i.e. 4-chlorobenzoate.

DESCRIPTION OF THE WORK

In order to set the parameters of the experiments, the study was first carried out in artificial soil microcosms contaminated with 4-chlorobiphenyl. A biphenyl degrader, *Pseudomonas* sp. B4, was introduced into the microcosm and its presence was checked by microbiological and molecular methods.

Despite a rapid degradation of 4-chlorobiphenyl, the toxicity of the soil remained very high against the tested biosensors, i.e. barley and earthworms. This toxicity was attributed to the dead-end metabolite of 4-chlorobiphenyl degradation pathway from *Pseudomonas* sp. B4, i.e. 4-chlorobenzoate. Moreover, when a 4-chlorobenzoate degrader, *Pseudomonas* sp. CBS3, was introduced into the microcosm, the toxicity against earthworms and barley decreased in correlation with the metabolization of 4-chlorobenzoate.

In this work, quantitative PCR was shown to be a useful tool to follow a bacterial population in soil. Quantification was realized by competitive PCR (Hallier-Soulier et al., 1996), and competitor sequences were constructed with the aim to detect *Pseudomonas* sp. B4 via a sequence of a *bph*C gene coding for a dihydroxybiphenyl dioxygenase and *Pseudomonas* sp. CBS3 via the gene coding for 4-chlorobiphenyl-dehalogenase. The DNA extraction method used sonication which destroyed free DNA and DNA released from dead cells. PCR was thus specially efficient when bacteria entered a viable but non culturable state.

The observation of the disappearance of 4-chlorobiphenyl in the microcosm should have lead to an assessment of soil detoxification. However, the results indicated that the accumulated 4-chlorobenzoate was as toxic against earthworms than the 4-chlorobiphenyl and even more toxic towards the growth of barley roots. This phenomenon argues in favor of the use of different methods, and particularly of ecotoxicological tests in order to estimate the innocuousness of a remediation process.

A second set of experiments was conducted with an unpolluted and non cultivated standard soil artificially contaminated with 4-chlorobiphenyl, in order to evaluate the bacterial behavior in a more complex system. The observations obtained with an artificial soil were amplified : when *Pseudomonas* sp. B4 was inoculated alone in the soil the accumulation of 4-chlorobenzoate resulted in total inhibition of barley growth. Only, the introduction of both strains allowed effective depollution of the microcosm.

MOBILITY OF TRACE ELEMENTS IN SOILS AND THEIR TRANSFER INTO CROPS

E. Podlešáková[1], J. Němeček[2]

[1] Res. Inst. for Soil and Water Conserv., Žabovřeská 250, 15627 Prague 5, Czech Republic
[2] Czech Agricultural Univ., Dep. Soil Science and Geology, Kamýcká 127, 16521 Prague 6, Czech Republic

Key words: Agriculture, arsenic, bioavailability, heavy metals, mobility, plants, sequential extraction procedure, soil contamination.

Soil reference values are being developed, which indicate adverse effects of potentially hazardous trace elements (HTEs) in soils for food chain and crop production. They will be based on studies of the HTEs mobility in soils and their transfer into plants, leading to critical crop loads from the viewpoint of food chain loading and phytotoxicity.

Mobilities of 12 potentially hazardous elements were studied by sequential analysis (20 samples; method by Zeilen - Brümmer, 1989) and by simplified speciation methods (260 samples; mobile forms: 1M NH_4NO_3 and 0.01M $CaCl_2$; potentially mobilizable forms: 0.025M Na_2EDTA; total content: $HClO_4$ + HNO_3 + HCl). Transfers into crops were investigated:

- in pot experiments with radish, spinach, barley, rye as testing plants,
- in field investigations of pairs soil/fodder plants.

Transfer experiments were running parallel to mobility findings. Studies were conducted on typical soil (Ap horizons) representatives of the soil cover of the Czech Republic, which have been contaminated in field conditions or which represent some geogenic extremes. The evaluation of some experiments with soils contaminated artificially serve for soil vulnerability assessments. Critical loads in crops (contents of HTEs determined in $HClO_4$ + HNO_3) are assessed in accordance with Czech national regulations and data in the literature (Vollmer 1995). Data are processed by standard statistical methods, by factor analysis and multiple regression analysis.

Soil-specific bounds of HTEs are characterised for both single HTEs (Hornburg, Brümmer 1991) and principal soil units and geogenic extremes of parent materials. Main features of the HTEs speciation in soil lithological units are reflected in:

- the dominance of the most strongly bound fraction (residuum in the sequential procedure) of Mn, Ni, Cr, Co, Zn, Cu in Cambisols from mafic parent materials and (especially Cu) materials in metallogenic zones,
- the high content of free-Fe-oxides-bound species of Zn and Cr in some Fluvisols and of As and Be in soils from geogenic extremes,
- the significant participation of organic bonds of Cd, Mn, Co, Zn, Ni, Cu in Chernozems and of Cd, As, Cu in some Fluvisols,
- the highest share of occluded species in Fluvisols.

Contaminated Soil '98, Thomas Telford, London, 1998, 961–962

From the ecological point of view the most important is the high ratio of mobile and mobilizable species of HTEs. The mobile fractions of Cd, Mn, Ni, Zn, Co are inversely pH-dependent. Mobile species are also increased in sandy soils especially in case of Cd. The factor analysis shows that the first factor loading reflect in this case the inversely pH-dependent mobilities and plant uptakes. Second (and also third in some sets) factor loading correlates with the total content and potentially mobilizable pool of HTEs. The analysis of some sets of data results in the conclusion that we have to prefer in predictions for this group of elements total, mobilizable and mobile species of HTEs and pH to indirect characteristics like texture, humus, free Fe and As oxides. The mentioned elements (and Cu) have the highest transfer factors (Cd > Zn > Ni > Cu) and therefore they can be harmful, mainly in acid soils. They are also taken up preferentially by plant accumulators. For these group of elements, especially Cd, Mn, Zn, Co, Ni we are able to derive for most soils multiple regressions, modelling the mobilities and crop uptakes, for example:

$$MN_{Cd} = 0.251\ ED_{Cd} - 0.056\ pH + 0.052$$
$$R_{Cd} = 5.436\ MN_{Cd} + 1.760\ TO_{Cd} + 0.092$$
$$MN_{Zn} = 0.073\ ED_{Zn} - 1.775\ pH + 0.013\ TO_{Zn} + 9.495$$
$$R_{Zn} = 5.467\ Mn_{Zn} + 0.616\ ED_{Zn} + 30.010$$

(for Cd and Zn: MN = mobile species in NH_4NO_3, ED = potentially mobilizable species in EDTA, TO = total content, R = radish; sig T < 0.05, IV = 56)

They will serve as prediction models for normsetting by matching the concentration of HTEs in crops with critical fodder and food plant loads and critical loads of phytotoxicity.

What concerns the other elements neither the first nor the second factor loading correlate with plant uptakes. Low ratio of mobile fraction is not inversely pH-dependent except of Pb or is positively pH-dependent - As, Cu. The transfer into crops is very low. From the comparison of the severely anthropogenically loaded Fluvisols with higher solubility of HTEs and soils derived from geogenic extremes with very low HTEs solubility we can conclude that due to their low transfers into plants soil contents 250 - 300 $mg.kg^{-1}$ for more soluble anthropogenic and 400 $mg.kg^{-1}$ (Cu, Pb), or even 1000 $mg.kg^{-1}$ (Cr) for slightly soluble geogenic loads do not cause surpassing of critical crop loads.

The field investigations provide us with more realistic lower crop uptakes, which are however affected by more interacting factors and are therefore less expressive.

The most important problem for setting reference values is the relevancy of critical concentrations in crops, which is beyond the scope of soil science.

References:

Hornburg, V. and Brümmer, G. W. (1991) Schwermetall - Verfügbarkeit und Transfer in Abhängigkeit von pH und Stoffbestand des Bodens, *Mitteilungen Dt. Bodendkundl. Gesellschaft, 661-664.*

Vollmer, M. K. (1995) *Herleitung und Anwendung von Prüf- und Sanierungswerten für schwermetallbelastete Böden in der Schweiz,* Eidgenössische Forschungsanstalt für Agrikulturchemie und Umwelthygiene (FAC), Schweiz.

Zeilen, H. and Brümmer, G. W. (1989) Chemische Estraktionen zur Bestimmung von Schwermetallbindungsformen in Böden, *Mitteilgn. Dtsch. Bodenkundl. Gesellsch. 59/I, 505-510.*

INFLUENCE OF SOIL TEXTURE ON HEAVY METAL MOBILIZATION IN SOILS PLACED IN ZONES WITH A SEMI-ARIDIC CLIMATE.

J.Martínez-Sánchez , C. Pérez-Sirvent , J.Vidal, M. Gil,.
Department of Agricultural Chemistry, Geology and Pedology, Faculty of Chemistry. University of Murcia, E-30071. Spain.
Key words: assessment risk, mobilization, heavy metal

A study on the natural mobility of Pb, Zn, Cr and Cd in polycyclic soils with argilic horizons in semi-aridic conditions (SE Spain) is presented. The soils studied (calcic Luvisols and luvic Calcisols) are dedicated to the cultivation of citrus trees. The soils are on a slight slope (0.6%) in the neighbourhood of an old mining site and so affected by heavy metal contamination arising from physical and physico-chemical transport of materials.
The mobility of both solid particles and soluble metal compounds above the argilic horizon is studied. The processes governing the transfer of heavy metals are strongly influenced by the semi-aridic climate, the presence of a high proportion of carbonates and the occasional but torrential rainfalls which, favoured by the Bt horizon's impermeability, transport heavy metals from the upper zone of the hill to the surrounding agricultural soils.

Materials and Methods. 12 samples were obtained from calcic Luvisols and luvic Calcisols soils within a 300 Ha sampling zone. In addition, fifteen sampling points were designated in the gullies and forty in the slags. The total metal content (Zn, Pb, Cr and Cd) was determined by electrothermal atomization atomic absorption spectrometry (ETAAS) or flame atomic absorption spectrometry (FAAS). To this end the samples were slurried in a dilute hydrofluoric acid solution and the suspensions were directly introduced into the flame or the electrothermal atomizer.
The water soluble fraction and that soluble in 10% HNO_3 were determined in both the slag and gully samples.
The selective extractants used for the soil samples were: DTPA; sodium dithionite + sodium citrate; HNO_3 0.1 M and HCO_3^- (1). The mineralogical composition of the samples was determined by XRD analysis using radiation Cu-Kα, and a semiquantitative analysis was made of the treated and untreated samples. The samples were also examined using a scanning electron miscroscope (SEM) instrument equipped with an EDS analyzer.

Results and Discussion.
In previous studies of soils of a sandy texture and subject to similar climatic conditions and mining influences, the conventional methodology commonly recommended to carry out mobility studies was shown to be inappropriate because of the presence of a high proportion of carbonates (2). This point was also confirmed in this study by means of XRD and SEM.
To evaluate the mobility of these metals and any risks involved in changing the use to which the land is put, Si Al, Fe and Mn were also determined in the extracts and a statistical study made of their correlation with the minority metals,Pb, Zn, Cd and Cr.

Metal mobility was assayed in a bicarbonate medium of pH 8.5, since this reagent mobilizes the plant available phosphorus fraction. The metals in the above assay would be easily mobilized in a carbon dioxide rich atmosphere and the bicarbonate medium would be similar to the bicarbonate environment of the soil solution in the rhizosphere. Even when the extracted fractions are in the order of 2-5%, these are mobilization conditions near those existing in carbonated soils. Indeed, the subterranean water extracted from nearby wells for irrigation purposes are rich in bicarbonate (40 meq/l). This phenomenon occurs when the soil has capillary water and indicates a real risk of metal mobilization.

Table 1. Analytical data of soil samples

	%Sand	%Silt	%Clay	O.M.	C/N	$CaCO_3$ Equiv	PH		ds/m
							H_2O	KCl	E.C.
Max	40	40	46	1.92	6.5	45	8.0	7.3	14.5
Min	28	25	32	1.15	5.1	4	7.5	7.3	4.2
Aver	35	32	40	1.55	7.7	30	7.9	7.3	11.2

Table 2. Mean values obtained from soil samples

	Total $mg*Kg^{-1}$	HNO_3 % ext	DTPA % ext	HCO_3^- % ext	M-J % ext
Zn	948	35	22	0.3	18
Pb	580	78	12	0.6	9
Cr	85	2	1	0.1	8
Cd	2	88	23	0.4	30

Table 3.- Mean values obtained from slag and gully samples

	Slags			Gullies		
	Total $mg*Kg^{-1}$	H_2O % ext	HNO_3 % ext	Total $mg*Kg^{-1}$	H_2O % ext	HNO_3 % ext
Zn	8000	65	80	5000	58	60
Pb	3500	2	60	2000	0.1	15
Cr	80	5	35	60	0.1	12
Cd	38	56	65	18	0.1	25

References

(1) Chapman, H.D., 1965. *In* C.A. Black, (Ed): *Methods of Soil Analysis, Part 2.* 891-900. Amer. Soc. Agronomy, Inc. Madison, Wis.

(2) Martinez- Sanchez, J., Perez- Sirvent, C. and C. Garcia Rizo. 1996. Errores de Evaluación de riesgos en la movilización de metales pesados en suelos carbonatados. *Actas III Congreso del Medio Ambiente.* pp. 1053-1101. Madrid.

Cu, Sn and Ge MOBILIZATION IN CALCAREOUS AGRICULTURAL SOILS PLACED IN ZONES WITH A SEMI-ARIDIC CLIMATE

C. Pérez-Sirvent, J. Martínez-Sánchez and C. García-Rizo.
Department of Agricultural Chemistry, Geology and Pedology. Faculty of Chemistry. University of Murcia, E-30071.SPAIN.
Key words: assessment risk, mobilization, heavy metal.

The aim of this work is to evaluate the risk of heavy metal mobilization in agricultural soils exposed to lead and zinc mining wastes. The mobility of both solid particles and soluble compounds of Cu, Ge and Sn are considered.The tin and germanium contents of soils are usually very low, which renders analytical determinations difficult. Consequently, there is little information in the literature regarding the biogeochemical behaviour and influence on the biotic chain of these elements.The soils studied are calcaric fluvisols developed from Quaternary alluvial sediments from the surrounding hills, some areas of which are dedicated to mining. The slag heaps, which are mixtures of mining wastes, mineral and rock, have undergone a process of supergenic alteration to give rise to secondary minerals such as kaolinite, smectite, alunite, jarosite, gypsum and a number of polyhydrated complex soluble sulphates of Zn, Mg, Fe, Mn, Al, Na and K, such as copiapite, halotrichite, botryogene, bianchite... These form solid solutions and incorporate smaller quantities of Ag, Ge, Sn, Pb, Cu,... (1). The processes governing the metal transfer from the element-rich zone to the neighbouring soils are strongly influenced by the semi-aridic climate, the presence of a high proportion of carbonates being an important factor in deciding which soluble metals are mobilized.

Materials and Methods.

Ten soil samples were obtained from a 5 Km^2 sampling zone. In addition, five samples were obtained from the main gully and thirty from the slags.
The total metal content was determined by electrothermal atomization atomic absorption spectrometry (ETAAS) or flame atomic absorption spectrometry (FAAS). For this, the samples were slurried in a dilute hydrofluoric acid solution and the suspensions were directly introduced into the flame or the electrothermal atomizer.
The selective extractants used were: water; 1 M ammonium acetate at pH 7.0 ; 0.5 M ammonium acetate + 0.02M EDTA + acetic acid at pH 4.65, ; 0.1 M sodium pyrophosphate, oxalic acid-oxalate; DTPA ; sodium dithionite + sodium citrate ; HNO_3 10% vv (2,3). In addition, an accepted sequential extraction procedure (4) based on three successive extraction stages was also applied to the same samples and the results were compared with those found using the above mentioned reagents. The mineralogical composition of the samples was determined by XRD analysis using radiation Cu-Kα, and a semiquantitative analysis was made of the treated and untreated samples. The samples were also examined using a scanning electron microscopy (SEM) instrument equipped with an EDS analyzer.

Results and Discussion.

The extraction values in H_2O (metal extracted x 100/ total content) point to the natural immobilisation of these metals when they are incorporated in carbonated soils, although these values diminish as one gets further from the source. The nitric acid extraction medium is a more aggressive medium than the mine acid waters and permits the

solubilization of the jarosite and alunite of the slags and their transportation to adjacent agricultural lands in the form of particulate materials

The incorporation of these minor elements to the soils is the consequence of three successive stages. The first step is the supergenic alteration process suffered by the mining wastes, which are sulphide-rich, to give rise to soluble sulphates. Next, because of occasional but torrential rainfalls, these sulphates are leached both as soluble compounds and as particulate materials. Finally, these acidic sulphate-rich lixiviation products are neutralized by the high proportion of carbonate present in the soils, the heavy metals being in this way immobilized in the soils. The results obtained by using the selective extractants agreed with the data obtained from the XRD and SEM studies of both the original samples and the residues remaining after each extraction stage.

Our data indicate that when dealing with samples with a high carbonate content, which are representative of aridic soils present in wide zones of the Mediterranean Basin, neither the sequential nor single extraction approaches provide a suitable extraction scheme. A reliable assessment of metal availability in these highly calcareous soils must take into account the mineral phase in which the metal is present.

Table 1. Mean values for all the samples studied

	Slag			Gully			Soil		
	Total mg/Kg	H_2O %Ext	HNO_3 %Ext	Total Mg/Kg	H_2O %Ext	HNO_3 %Ext	Total Mg/Kg	H_2O %Ext	HNO_3 %Ext
Cu	650	20	60	230	0.4	10	180	0.3	25
Ge	140	8	48	112	<0.05	<0.1	83	<0.05	<0.1
Sn	350	3	30	118	<0.05	1	79	<0.05	0.2

Table 2. Mean values obtained for the soil samples using the selective extractions (solublex100/total) and sequential procedure (three stages)

	1 Stage	2 Stage	3 Stage	NH_4Ac	EDTA	DTPA	Oxal	Cit-Dit	Pyro
Cu	10	8	12	1.2	1.9	14.0	9.0	19.0	4.4
Ge	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1	2	3
Sn	0.5	0.5	2	<0.1	4	<0.1	59	58	60

REFERENCES

(1) Lopez-Aguayo, F., Pérez Sirvent, C., Ortíz Gonzalez, R., Arana, R., 1992. Composición química de las aguas de lixiviación minera en el Cabezo de San Cristobal (Mazarron, Murcia). *Rev* Rev. Soc. Geol. España. 5, (3-4),73-79.

(2) Perez-Sirvent, C., Martinez- Sanchez, J. and C. Garcia-Rizo, Assessment of the risk of heavy metal mobilization in calcareous agricultural soils in *Proceedings of the Third International Conference on the Biogeochemistry of Trace elements.* In press.

(3) Chapman, H.D., 1965. *In* C.A. Black, (Ed): *Methods of Soil Analysis, Part 2.* 891-900. Amer. Soc. Agronomy, Inc. Madison, Wis.

(4) Ure, A.M., Quevauviller Ph., Muntau, H, and Griepink, B., 1993. Speciation of heavy metals in soils and sediments. Intern. J. Environ. Anal. Chem., 51, 129-134.

THE EFFECT OF SOIL COMPACTION ON SEED EMERGENCE FROM AN INDUSTRIAL SOLVENT CONTAMINATED SOIL

Turlough F. Guerin[1], Anna Harrison[2] and Patrick M. Guerin[3]

[1] *Rio Tinto, Research and Technology Development, Environmental Technology Division 1 Research Avenue Bundoora, 3083, Victoria, Australia, fax (61) 3 9242 3222, E-mail: Turlough.Guerin@riotinto.com.au (main author)*
[2] *University of Melbourne, Parkville, 3052, Victoria, Australia*
[3] *3 Cupro St. Lithgow, 2790, New South Wales, Australia*

Keywords: Bioremediation, Contaminated Soil, Case Study, Phytoxicity, Clay, Solvents, Deep Compaction

SUMMARY

An increase in bulk density of soil, resulting from loads applied for short periods, is referred to as compaction. Compaction of a soil may adversely affect air and water movement, seedling emergence and root penetration. Changes in bulk density are used as a measure of soil compaction. When a soil is subjected to a load, the bulk density it will reach depends upon its particle size distribution and its water content. For the soil studied, soil compaction and residual solvents in the soil both influenced seed emergence and early plant growth for Thrift and Blackbutt oats. The response to soil physical and chemical conditions varied between the two species. Emergence and growth of Thrift showed greater sensitivity to increasing soil compaction, although soil contamination may reduce the emergence of these seeds. At higher levels of compaction, Thrift root and shoot growth appear to be restricted.

INTRODUCTION

The ability of the plant root to find space in which to grow or force its way into the soil is often the most important factor limiting plant growth. Primary plant roots are usually larger than many of the pore spaces available to them, especially in compacted soils. Therefore, roots must force their way into soils, so they can only grow in soils which are compressible. Roots will rarely enter a light textured soil if its bulk density exceeds 1.7 to 1.8 gcm^{-3} or a heavy-textured soil if it exceeds 1.5 to 1.6 gcm^{-3} (Russell, 1973).

It is possible that large seeded plants, such as peas which have a well developed tap root, can exert a maximum pressure as high as 5 or 10 bar, but cereal roots tend to have their growth restricted by much smaller soil pressures. However, other studies have shown that particular cultivars of oats *(Avena sativa)* can grow under a wide range of soil compaction and water logging conditions (Guerin and Guerin, 1992a,b; 1993).

The reported ability of confined roots being capable of exerting pressures of up to 10 bar may explain the ability of roots to eventually penetrate compacted zones, as well as their ability to penetrate, and enlarge cracks and crevices in rocks, roads and foundations. However, from an agricultural point of view, minimising soil resistance to root elongation rather than mobilising maximum root pressure is of greater interest (Hillel, 1982). At any given bulk density, resistance to root penetration is inversely proportional to moisture content. However, roots often fail to penetrate wet soils that may be mechanically penetrable, owing to the effects of reduced oxygen supply which may not meet the plant's requirements for growth. In dry periods, adequate oxygen may be available, but the soil strength may increase so that roots still cannot penetrate the soil. In wet periods, no significant reduction in yield may occur, but yields may decrease under dry conditions. The bulk density at which root penetration stops varies with soil texture, soil water content and plant species.

Previous research has shown that roots are unable to decrease in diameter to enter pores narrower than their root caps. Therefore, if they are to grow through compacted soil they must displace soil particles to widen the pores by exerting a pressure greater than the soil's mechanical strength.

In addition to this, compaction also restricts movement of water and air through a soil by reducing the number of large pores, placing roots under several simultaneous stresses (Hillel, 1982).

Where soil is highly compacted, root growth may be restricted almost entirely to cracks and cleavage planes. In seeking out these zones, plant roots are not merely passive agents, as they promote differential shrinkage through preferred extraction of moisture from zones of greater penetrability (Hillel, 1982). When root growth is restricted by soil compaction, total plant biomass and crop yield are usually also reduced.

METHOD

Soil samples (medium to heavy clays) were collected from a site known to be highly contaminated with industrial solvents (Rhodes and Guerin, 1996). Thrift *(Ameria maratima)* and Blackbutt oats *(Avena sativa)* were used in the trial. One contaminated soil and one uncontaminated soil (from the same site) were used and these were compacted from 100-800 psi for a series of bulk density, soil strength, germination, seed emergence, shoot and root length trials.

RESULTS AND DISCUSSION

For the soil studied, soil compaction and soil chemical contaminants both influenced seed emergence and early plant growth for Thrift and Blackbutt oats. The response to soil physical and chemical conditions varied between the two species. Emergence and growth of Thrift shows greater sensitivity to increasing soil compaction, although soil contamination may reduce the emergence of these seeds. At higher levels of compaction, Thrift root and shoot growth appear to be restricted. Germination and emergence of Blackbutt oats was substantially different under conditions of increasing compaction. Although plant growth of Blackbutt oats appeared to be little affected by increasing soil compaction, shoot and root length was reduced. Blackbutt oats were more adversely affected by the residual contamination in the soil than by increases in soil compaction. Emergence and growth of Thrift shows greater sensitivity to increasing soil compaction, although soil contamination may reduce the emergence of these seeds.

REFERENCES

Hillel, D., (1982) Introduction to soil physics, Academic Press, Inc. (London) Ltd, London.

Guerin, P.M, and Guerin, T.F. (1992) "Breeding oats for irrigation". Proceedings of the 4th International Oat Conference. Eds. Barr, A.R., R.J. McLean, J.D. Oates, G.Roberts, J. Rose, K. Saint, Vol III, *187-190.*

Guerin, P.M., and Guerin, T.F. (1992) "A Rapid low technology method of breeding high yielding oats with dual purpose characteristics". In Proceedings of the 4th International Oat Conference Eds. Barr, A.R., R.J. McLean, J.D. Oates, G. Roberts, J. Rose, K. Saint, Vol III, *191-195.*

Guerin, P.M. and Guerin, T.F. (1993) "Breeding more than single-purpose oats". Journal of the Australian Institute of Agricultural Science *6, 25-26.*

Kelly, R.J., and T.F. Guerin (1994) "Metal Accumulating Plants and Implications for the Mining Industry" Australian Journal of Mining, *pp38-40.*

Guerin, T.F., and Kelly, R.J. (1994) "The advantages of using plants for bioremediation of mine sites, mine wastes and other contaminated land: soil structure reclamation, accelerated biodegradation and hyperaccumulation". Economic Growth with Clean Production - Transfer of Cleaner Production, Pollution Control and Energy Conservation Technologies. CSIRO and UNIDO, Melbourne, 7-10 February.

Rhodes, S.H. and T.F. Guerin (1996) Bioremediation of Petrochemicals after the Coode Island Fires. pp. *11.* International NATO/CCMS Conference, Adelaide.

Russell, E.W., (1973) Soil conditions and plant growth, 10th ed., Longman Group Limited, London

Tennant, D., (1975) A test of a modified line intersect method of estimating root length, Journal of Ecology, 995-1001.

Hydraulic in-situ Remediation Techniques with Surfactants: Optimization of Hydraulic Systems

REINHOLD JOSEF, BALDUR BARCZEWSKI, HANS-PETER KOSCHITZKY, JÜRGEN BRAUN
VEGAS, Institut für Wasserbau, Universität Stuttgart, Pfaffenwaldring 61, 70550 Stuttgart, Germany

Keywords
behaviour of contaminants, trichloroethylene, in-situ groundwater remediation, heterogeneity, large-scale experimental basin, removal rates, tracer

Problem

Conventional pump and treat methods, most frequently used for the clean-up of contaminated aquifers, are only suited for the extraction of the contaminated plume downstream the pollution source. Due to the often very low solubility of the contaminants and the inhomogeneities of the subsurface, the efficiency of pump and treat methods can be rather low and remediation times may exceed decades.

Objectives

- Development of improved hydraulic remediation systems for the extraction of contaminants at the source (optimization of hydraulics)
- Improvement of the uniformity of the flow through inhomogeneous aquifers, using specially designed wells
- Determination and minimization of the permeability reductions induced by surfactants
- Use of surfactants in technological scale to enhance the solubilization and mobilization of the pollutants
- Minimization of consumption and costs of surfactants and energy
- Development of special systems for waste water treatment and the recovery of surfactants

Technological Experiments

An artificial inhomogenious aquifer with the Dimensions 9 x 6 x 4.5 m (L x W x H) was designed and constructed. It consists of 60 discrete blocks of different permeability, each block with one kind of sand.

Tracer tests were combined with the numerical model "SICK 100" to estimate in detail the "real" permeability of the emplaced sands. While comparing the measured and the predicted breakthrough times in the aquifer deviations due to inhomogenities were established.

Procedure of the first remediaion experiment:

- Emplacement of a zone of residual TCE while the ground water table was lowered just below source zone (source bulk volume: 1.68 m^3, total mass of TCE emplaced: 29.3 kg).
- Raising of ground water level
- Installation of full screened remediation wells equipped with packer systems
- Start of remediation during ground water flow with a hydraulic gradient of 0.5 %
- Continuous measurement of flow rate and TCE concentration in groundwater effluent and extraction wells.
- Optimization of the remediation through adaption of the hydraulic system (rate and location of removal / injection)

Results

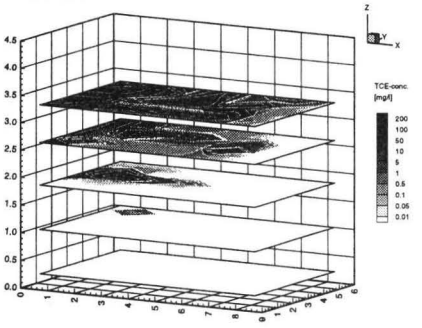


Fig. 1: TCE-Distribution after initial rising of the ground water table.

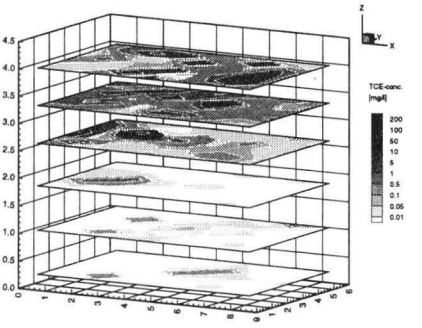


Fig. 2: TCE- Distribution after 8,5 weeks of pumping.

- Figures 1 and 2 are based on 378 sampling locations. High-Pressure-Liquid-Chromatography was used to determine the TCE-concentration in the samples
- After 20 days of hydraulic remediation, approximately 22 kg of TCE were removed from the pumping well. From the groundwater leaving the aquifer at the constant head outflow, approximately 2 kg of TCE was removed additionally (Fig. 3, Fig. 4).

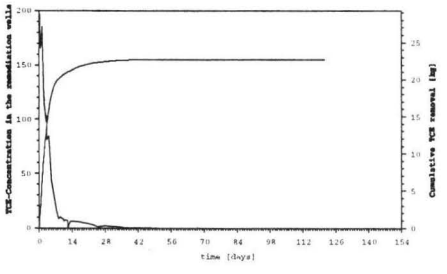


Fig. 3: TCE concentration and cumulative TCE removal in the remediation wells.

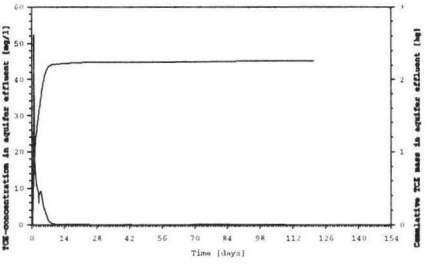


Fig. 4: TCE concentration and cumulative TCE removal in the aquifer effluent

- Less tailing than in conventional pump and treat systems is expected due to adjustment of flow rate and flow direction.

Outlook

Similar large scale experiments will be carried out in different artificial aquifer structures and other contaminants (LNAPLs) while using surfactants.

The results of every large scale experiment will be compared with other hydraulic remediation techniques (ground water circulation well, air injection well) which were used in the same aquifers with the same starting conditions.

The Influence of different parameters on the permeability reductions induced by surfactants will be quantified by additional column experiments

The calibration of the numerical modell will be completed using the tracer break through curves and the measured piezometric heads at 378 points.

SUBSURFACE FATE AND TRANSPORT OF GASOLINE OXYGENATES

Bruce J. Bauman, Soil & Groundwater Research Program Coordinator
American Petroleum Institute, 1220 L Street NW, Washington, D.C. 20005

Key Words: behaviour of contaminants, soil and groundwater contamination

Alkyl ethers have been used as blending components for gasolines since the 1970's. They are used both to increase octane and to provide lower vehicular emissions. Their use in the United States has increased substantially over the last decade with the phase out of leaded gasolines and the implementation of state and federal regulations requiring new formulations of gasolines that will provide reduced vehicular emissions. These regulations mandate the amount of oxygen in gasolines, and the alkyl ethers, along with ethanol, have been found to be the best compounds for use in these gasolines. Worldwide production and use has also been growing rapidly as regulatory agencies in other countries seek reductions in the use of organolead compounds commonly used in leaded gasoline. Methyl tert butyl ether (MTBE) is the most commonly used alkyl ether, and currently ranks third in terms of U.S. organic chemical production.

The environmental behavior of oxygenated gasolines when released to soil or groundwater has been the topic of heightened interest, and has been summarized in several recent papers (Zorgorski et al., 1997; Squillace et al., 1997). While abundant literature exists describing the relevant transport mechanisms and remediation technologies for the monoaromatic hydrocarbons that are typically the focus of risk assessment and remediation efforts, there are far fewer reports addressing MTBE or other alkyl ethers. The American Petroleum Institute (API) has been conducting field and laboratory research on these compounds since 1983, and has recently published two studies documenting the intrinsic remediation of MTBE (API, 1997a&b; Borden et al., 1997; Schirmer et al., 1997). These studies used different techniques for obtaining a mass balance of contaminant flux, as well as companion laboratory studies. Both field studies conclude that biodegradation played a major role in MTBE mass loss, although laboratory data did not always match the field results. Additional studies underway which will clarify the initial results at these two sites.

Another study is in progress to characterize the MTBE plumes at over 400 underground storage tank (UST) sites in the state of Texas. This work will use the same approach as a previous study that characterized benzene plumes (Mace et al., 1997). Data has been collected that describes the source area for these plumes, as well as maximum MTBE concentrations and changes of concentration with distance from the source. The study should be completed by late summer of 1998, and generate a much clearer picture of the role of natural attenuation in MTBE groundwater transport.

Two additional field studies have been initiated in early 1998 to evaluate site characterization techniques and the intrinsic biodegradation of MTBE at gasoline release sites. One study will involve the injection of deuterated MTBE into an existing dissolved BTEX and MTBE plume. The subsurface microorganisms at this site have

had at least several years of exposure to MTBE which may enhance the potential for biodegradation. Another study is in the initial stages of identifying sites that could be candidates for long term (several years) research to characterize MTBE plumes and natural attenuation.

Lab column and batch reactor studies have been started to better understand the mass flux of dissolved MTBE from residual sources at the water table. In a unique controlled release study in a model aquifer (10x5x10m) scheduled to begin in mid-1998, an oxygenated gasoline will be released, the development of the dissolved plume characterized, and the mass removal effectiveness of air sparging will be characterized.

When evaluating possible ground water impacts, the solubility and biodegradability of MTBE and the alkyl ethers are of greatest importance. Their dissolved concentrations in groundwater may be relatively high, especially if reformulated or oxygenated fuels (containing 11% vol. and 15% vol., respectively) are spilled. Since their apparent biodegradability is much less than BTEX, these dissolved plumes have the potential to migrate further from the site than BTEX. When dissolved in water, MTBE is considerably more difficult to remove than BTEX compounds with conventional technologies.

The taste and odor thresholds for MTBE and other alkyl ethers in water are low (20-40 ug/L), and are far below the concentrations considered to have health effects due to chronic exposure. Like other components of motor fuels, MTBE may occur frequently in stormwater or surface water, but the reported concentrations are very low, and would not be expected to have a detrimental effect on ground water quality.

API. 1997a. Field Studies of BTEX and MTBE Intrinsic Bioremediation. Publ. #4654. American Petroleum Institute, Washington, D.C.

API. 1997b. Delineation and Characterization of the Borden MTBE Plume: An Assessment of MTBE Transport in Groundwater Over 8 Years. Publ. 4668. American Petroleum Institute, Washington, D.C.

U.S.EPA. 1997. Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on MTBE. EPA Office of Water, Wash. DC. Publ. #EPA-822-F-97-008.

Borden, R.C. R.A. Daniel., L.E. LeBrun IV and C.W. Davis. 1997. Intrinsic Biodegradation of MTBE and BTEX in a Gasoline-Contaminated Aquifer. Water Resources Research, 33(5):1105-1115

Mace, R.E., R.S. Fisher, D.M. Welch, and S.P. Parra. 1997. Extent, Mass and Duration of Hydrocarbon Plumes from Leaking Petroleum Storage Tank Sites in Texas. U. Texas Bureau of Econ. Geology, Geol. Circ. 97-1.

Schirmer, M., J.F. Barker, and C.E. Hubbard. 1997. Study of the Long-term Attenuation of MTBE at the Borden Field Site, Ontario, Canada. (*In press*, Ground Water Monitoring and Review)

Squillace, P., J.F. Pankow, N.E. Korte, and J.S. Zogorski. 1997. Review of the Environmental Behavior & Fate of MTBE. Env. Tox. & Chem. 16(9):1836-1844.

Zogorski, J.S. et al. 1997. Fuel Oxygenates and Water Quality - Current Understanding of Sources, Occurrence in Natural Water, Environmental Behavior, Fate and Significance. Office of Science and Technology Policy, Washington D.C.

THE VERTICAL MIGRATION OF RADIONUCLIDES IN THE SOILS AFTER THE CHERNOBYL ACCIDENT

E.V.Kvasnikova, A.N.Pegoev, E.D.Stukin

Institute of global climate and ecology, Glebovskaya str., 20-B, 107258 Moscow, Russia

Key words: radioactive contamination, radionuclides

Interest for vertical distribution of radionuclides in the soils, for variations in their spatial distribution and with time, is connected with the fact, that these data stipulate radiation levels on the surface of the earth, penetration of the isotopes into plants and animals, their transit into underground water, and washoff by surface water. The main characteristic features of radiation situation over a contaminated area are contamination levels and vertical migration of the radionuclides. Studies of changes in the distribution of the radionuclides with depth (profiles) with time, i.e.their migration into the soil, were carried-out for some decades (Pegoev, A.,1980). However, because the process of their transit is complicate and stipulated by many factors, numerous available data of experimental observations, experiments and derivations of a theory do not compile complete and non-contradictory picture. In this connection, it seems to be useful to analyse a vast data set observed in the Chernobyl NPP zone.

The goals of the study of the radioactive contamination of soils by layer sampling, are the following:

- to detect the level and composition of the contamination, characterised by certain radionuclide store, i.e. by activity corresponding to unit area in the integral over the depth (kBq/m^2);
- to detect deep profiles of the radionuclides in the soil, i.e. a relationship between their contents or store in certain layers and the depth;
- to detect a relationship between the profiles and periods of time, to estimate the rate of migration in mechanically sacred soils, to study its connection with the soil type, climatic and hydrological regimes.

The above mentioned goals are subordinated to the aim of adequate description of the radiation situation over the contaminated areas, and to forecast its changed in time. This study discusses some results of gamma-spectrum analysis of some series of soil samples from the zone contaminated from the Chernobyl accident.

At first, there are 65 multilayer samples, taken in 1986-1990 within ten typical landscape-geochemical areas, located in Mogilev, Gomel, and Kiev districts. Sampling was repeated for 2-5 times in some sites. Caesium-134 and caesium-137 contents (expressed as their stores within each layer, in kBq/m^2) were measured with the help of laboratory gamma-spectrum analysis.

At second, 147 11-layer samples were studied, taken in 1991 in 49 sites, characterised by considerable contamination levels (three samples from each site). The sites were situated near permanent observation points, established along 36 azimuths (each 10^o, 1-10 km distant from the damaged unit of the CNPP). Cerium-144, stibium-125, ruthenium-106, caesium-137, and caesium-134 contents were measured within each layer, using the gamma-spectrum method.

At third, there are 11 multilayer samples from the Tula region caesium spot (Russia) taken in 1996-97 under INTAS-RFBR project 06-95-1249.

Contaminated Soil '98, Thomas Telford, London, 1998, 973–974

The observed deep profiles of the radionuclides distribution in the soils can be subdivided into three types: a) exponential; b) more bulged than exponential; c) exponential ones, or more bulged than exponential, with a pellicle of radionuclide at the surface. Concave profiles with the pellicle are a characteristic feature of caesium. As to the other elements, the exponential profiles prevail.

It is convenient to approximate the profiles by exponents and to characterise them by the parameters of the exponent, namely, the total store and penetration constant, as well as the mean depth of radionuclide migration into the soil.

Evolution of the profiles can not be detected, comparing the results of the repeated sampling in the same sites, because of considerable variability in the store and vertical migration within the same site.

The character of the profiles does not depend on the contamination age (it was from 3 months to 11 years in this series of samples). This makes possible to suggest the profiles were formed for a short period of time after the deposition, and than they changed slowly.

Difference in the vertical migration of caesium of explosive and reactor origin was estimated on the base of soil samples series with moderate contamination level, taking into consideration the difference in the vertical migration of different caesium isotopes. According to these estimations, the vertical migration of global caesium-137 fallout (25 years old) is 5 times as great as this one of the Chernobyl products. However, most probably, this difference is stipulated by mechanical disruption of the soil for the period preceding the Chernobyl accident.

Studying vertical migration of cerium-144, stibium-125, ruthenium-106, caesium-137, and caesium-134, we observed that variability of the vertical migration of stibium-125 (and, to some extent, of ruthenium-106) did not conform to those of the other radionuclides. It was a characteristic feature of sandy soils. In peat and clayey soils this process was not so pronounced. The correlation between stibium profiles and those of the other radionuclides was not significant, in spite of the soil type.

As to the composition of the contamination, the sampled sites can be distinctly subdivided into two groups. Constant ratio between the radionuclides was observed within each group. The first group (in comparison with the second one) is rich in caesium-137 (12 times), stibium-125 (7,5 times), ruthenium-106 (2,8 times) relative to cerium-144. We suggest the groups of sites belong to different patterns, where the products generated by different temperature regimes, were deposited (Kvasnikova, E. et al., 1994).

REFERENCES

Kvasnikova, E., Pegoev, A., Stukin, E., Fridman Sh. (1994) Analisis of the results of the radioactive contamination of soils in Chernobyl NPP zone by gamma-spectrometry of stratum samples techniques. In: The techniques and the certain results of the airborn-gamma-spectrum survey of the radioactive contamination of the European part of Russia. Sankt-Peterbourg: Hydrometeoizdat, p.206-224.

Pegoev, A. (1980) The practical methods of the data treatment in the applied gamma-spectrometrie. Leningrad: Hydrometeoizdat, 160 p.

HEAVY METAL CONTAMINATION IN URBAN SOILS

F.Bretzel, L.Lubrano, G.Petruzzelli
Inst. of Soil Chemistry, C.N.R., *via Corridoni 78, 56125* Pisa, Italy

keywords:heavy metals,lead, quality of the soil, urban areas, zinc.

Introduction

The presence of green areas in towns has become important in recent years because they are directly linked to quality of life. It is known that plants have a role in controlling the temperature in town, that is higher than in the surrounding country areas. Plants also help in protecting from sun irradiation, from wind and high temperatures by the action of evapotranspiration. Green areas reduce noise levels and atmosphere pollution: the leaves absorb dust, pollutants and CO2 in excess. The quality of soil in towns is often bad. Urban soils are generally constituted of a very broad range of materials, and they are characterised by being asphyctic, unstructured and lacking in nutrients, compared to natural soils. They are often heavily contaminated by several pollutants. Among them heavy metals as Cu, Zn, Pb, Cd, Cr, Ni play an important role. They come from several sources: industrial waste, combustion processes, building materials and vehicular traffic. The research was carried out to evaluate the quality of the soil and the consequent effects on plant health. It has sprung from the need to preserve green areas and citizen health (Sheppard and Evenden, 1994) and one of the aims is to evaluate the effects on vegetation and find possible peculiar behaviour in towns' plants like accumulation or exclusion of heavy metals (Baker, 1981).

Materials and Methods

Heavy traffic roads of the centre and the suburbs were chosen as areas for sample collection. We analysed soils and vegetation, herbaceous species and trees. In the herbaceous lawn species we divided leaves from roots and analysed them separately. All plants have been carefully washed in distilled water.

We collected samples in the town's Botanical Garden, that we intended to consider as a control sample.Plant and soil samples were dried at 105°C, and digested with HNO_3 - $HClO_4$ in a microwave oven. They were analysed for Pb, Cd, Cu, Zn, Cr, Ni by Atomic Absorption Spectroscopy (Perkin Elmer 3030, equipped with the background corrector). Metal speciation was carried out by a sequential extraction procedure with H2O, KNO3 and EDTA (Petruzzelli *et al.*,1993).Some important soil characteristics like pH and organic matter were determined and they respectively resulted near neutrality or slightly alkaline (7-8) and about 6-8%.

Results and discussion

Among the results obtained in this preliminary study we reported some in the tables 1 and 2; they show the values founded in different areas.

SOIL	Cu	Zn	Ni	Pb	Cr
Total	52.5	82.5	42.4	225	35.0
KNO_3	1.0	0.5	1.0	2.0	0.01
EDTA	12.4	15.0	1.6	57.5	0.03
PLANTS					
Lawn					
roots	27.5	127	10.1	47.5	15.7
leaves	25.5	117	10.0	50.0	12.1

Table 1 Heavy metal in soils and vegetation . Data is in mg/kg dry weight at 105°C.

SOIL	Cu	Zn	Ni	Pb	Cr
Total	77.5	85	60.0	145	62.5
KNO_3	1.0	0.5	1.1	1.5	0.01
EDTA	20.2	7.5	1.5	45.1	0.06
PLANTS					
Lawn					
roots	32.5	95.5	10.1	40.2	10.3
leaves	17.5	62.5	5.0	20.0	9.9
Linden					
leaves	7.6	30.0	7.5	10.4	2.7

Table 2 Heavy metal concentration in soils and vegetation. Data is in mg/kg dry weight at 105°C.

of the town. In all the samples the Cd content is under 0,1 mg/kg.

At this stage of the research we can conclude the following:

- All the soil revealed a relevant presence of Pb and Zn: some of them reached a noticeably high level. The amount of Cd is negligeble,while Cu, Ni and Cr have been found in normal quantity (Petruzzelli and Barbafieri, 1995)
- Highest levels of Pb were noticed in soils located on their site for many years, that could be related to the fact that Pb is not very mobile. On the other hand, recent filling grounds, even near high traffic roads, showed a low quantity of metals.
- The samples collected in the Botanical Garden showed high levels of contamination, especially due to Pb and Zn; the data suggests the need to deepen the research in that area, to define the possible sources of pollution: as the Garden is quite isolated from traffic, we will not exclude the possibility of contamination from the water bearing stratum, because in Pisa it is very high (at some points 30-40 cm).
- In some city areas also the concentration of mobile species of heavy metals in soil is particularly relevant, as in the case with lead. These levels indicate a high contamination of soil, suggesting the existence of potential health hazards.
- As regards vegetation, we had interesting results particularly in herbaceous plants (mainly Graminaceae), where we found Pb in noticeable quantity in the roots. In trees the amount of Pb is low.
- Beyond the effect of traffic, the very broad range of materials which constitute the soils of urban areas, can contribute to the low level of soil quality.

In the next phase of our research we intend to analyse wood tissues from urban trees and start an experimental trial on the same species in controlled environment.

References

Baker A..J..M.1981. Accumulators and excluders- strategies in the response of plants to heavy metals. "Journal of Plant Nutrition" 3: 643-654.

Sheppard S.C. and Evenden W. G.1994. Contaminant enrichment and properties of soil adhering to skin. "Journal of Environmental Quality" 23: 604-613.

Petruzzelli G., Lubrano L., Giovannini G., Lucchesi S., Cervelli S. 1993. Distribution and behaviour of heavy metals in soils following different clean up procedures. F.Arendt et al Eds "Contaminated Soil" 545

Petruzzelli G. and Barbafieri M. 1995. Qualita' del suolo e problemi di identificazione dei siti contaminati Rifiuti urbani e industriali. A. Frigerio Ed. GSISR Milano

SPECIATION OF NICKEL IN NATURAL AND CONTAMINATED SOILS. POTENTIALITY OF PHYTOREMEDIATION

M. Barbafieri, L. Lubrano and G. Petruzzelli
Institute of Soil Chemistry, CNR, Via Corridoni,78 - 56125 Pisa, Italy

Key words: Nickel, chemical speciation, risk analysis, quality of the soil, soil/plant transfer

Introduction

The main source of environmental contamination of Ni are: refineries, industrial or municipal wastes and auto emission but in many cases, in Italy, Ni is present in very high concentration also in natural soils (over 300 mg/Kg). So it is necessary to ascertain these phenomena from cases of environmental pollution. Mobility of Nickel in the soil environment is the essential feature to distinguish between natural and anthropogenic sources. In this work Ni speciation in natural (A, B) and polluted soils (C,D with similar total concentrations) was studied. Mobile species was determined with a simplified procedure of sequential extraction: H_2O, KNO_3, DTPA (Petruzzelli *et al.* 1993) to evaluate water soluble, exchangeable, and complexed/adsorbed species. At laboratory scale also a study of plant uptake was carried out according to Petruzzelli *et al.* (1986), in order to evaluate the relation between mobile species and phytoavailability. Alfalfa (*Medicago sativa L.*) was selected for its tolerance at high level of heavy metal concentration in soil and also to verify its effectiveness in phytoremdiation technique.

Extraction	NATURAL SOIL		SPIKED SOIL	
	A	B	C	D
Total	103	365	100	300
H_2O	ND	0.5	0.5	0.5
KNO_3	2.5	2.5	3	12
DTPA	1	5.5	18.5	76.5

Table 1. Total and chemical mobile forms concentration (mg/kg) of nickel in different soils.

Chemical distribution of Ni in soil and its importance in environmental risks evaluation.

In table 1 data on Ni contents and speciation is shown. Even if total content is similar, the distribution of the metal in the mobile species is quite different. The most important differences are between KNO_3 extraction (exchangeable species) and DTPA extraction (complexed/adsorbed species). The comparison between samples with similar total concentration, shows that DTPA nickel extractable between A and C increased 18 fold and between B and D increased 14 fold. The results are also compared with tables of three level risk based on the characterisation of mobile species in Italian soils (Barbafieri et al. 1996). The results obtained are reported in figure 1. The large difference in the hazard evaluation among natural and spiked soils is quite evident, even if the total concentrations are very similar. Both A and B, natural soils, have Ni-DTPA below the trigger level, on the contrary C is over the trigger level and soil D is even over the intervention limit.

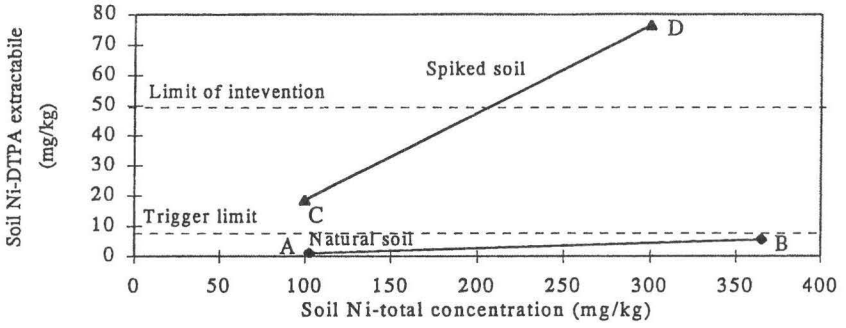


Figure 1. Nickel total concentration vs nickel DTPA-extractable. Natural spiked soils in relation to difference levels of risks.

Ni accumulation in *Medicago Sativa L*

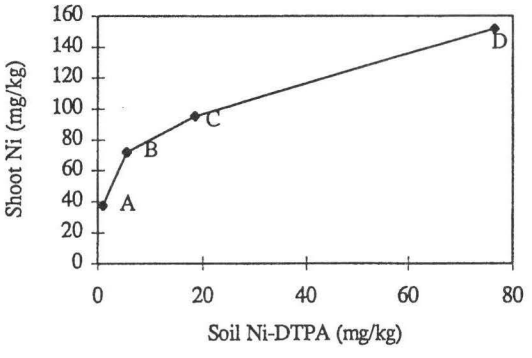


Figure 2. Nickel accumulation by Alfalfa and Ni-DTPA concentration in different treatment. (A;B natural soil and C,D spiked soil)

Alfalfa is recognized as good metal tolerant and metal accumulator species and is proposed as a plant for bioremediation of heavy metal contaminated soils (Canarutto 1995). In figure 2, the results are shown on plant Ni uptake in relation to Ni-DTPA extractable. The data shows a good correlation between Ni uptake and Ni-DTPA. At the highest concentration of Ni in soils phytotoxic symptoms were evidentiated by reduced biomass production.

The results stress the need of evaluation of Ni mobile species in order to evaluate the environmental risks correctly and to define the real hazards at heavy metal contaminated sites. Plant uptake showed the high correlation with mobile species (Ni-DTPA extractable) indicating the low significance of the total content to define bioavailability of the metal and its possible transfer into the food chain and the potentiality to use the sequential extraction procedure. Alfalfa confirms the capacity to tolerate and accumulate very high Ni concentration.

References

Barbafieri M., Lubrano L. and G. Petruzzelli. Characterization of pollution in sites contaminated by heavy metals. Annali di Chimica, 86: 585 - 594 (1996).

Canarutto S. Decontamination of heavy metal-contaminated soil by the growth of medicago sativa L.: laboratory trials. Fresenius Env.Bull. 2: 711-716 (1993).

Petruzzelli G., Lubrano L., and S. Cervelli. Heavy metals uptake by wheat seedlings grown in fly ash amended soils. Water, Air and Soil Pollution, 389 - 395 (1986).

Petruzzelli G., Lubrano L., Giovannini G., Lucchesi S. and Cervelli S. Distribution and behaviour of heavy metals in soils following different clean-up procedures. F. Arendt et al Eds "Contaminated Soil" 545-4((1993).

CHARACTERISATION OF HEAVY METALS MOBILITY IN ABANDONED MINING AREA IN SARDINIA (ITALY)

[*]M. Barbafieri , [§] C. Dadea

[*]*Inst. of Soil Chemistry, National Research Council, Via Corridoni 78, 56100-Pisa, Italy*

[§]*Dep. of Earth Science, Univ. of Cagliari, Via Trentino 51, 09127-Cagliari, Italy*

Key words: chemical speciation, risk analisys, mining, abandoned polluted area, remediation, soil/plant transfer, remediation

Introduction

Mining sites are among the most dangerous for chemical contamination due to the large amounts of toxic metals. In fact abandoned tailings can spread contaminants in near areas and can adversely affect on soil, water and wildlife. The area under study is an abandoned mine site locate in south-western Sardinia (Italy). The recent dismantling of all mining activities has dramatically increased Pb, Zn and Cd contamination in surface waters (Caboi et al.1994). Within the mine tailings area, only isolated patches of grasses exist. In order to evaluate the degree of pollution in sites surrounding mine tailings, it is starting a monitoring research with the goal to know the diffusion of heavy metals and the hazards for the environment. Samples were collected near and far from mine tailings.

The total concentration in contaminated sites represents the starting point in order to evaluate the degree of pollution. For this reason, in this work, preliminary results are reported of analysis of heavy metals mobility using a simplified procedure of sequential extraction: H_2O (water soluble fraction), KNO_3 (linked with electrostatic forces, exchangeable fraction), EDTA (linked by covalent forces, complexed/adsorbed fraction. Then, results are compared with a model of three level risk for hazard evaluation based on the mobile species obtained with the sequential extraction mentioned above (Barbafieri et al.1996).

Results and Discussion

Mineral samples

The mobile species of Pb, Zn, Cd are quite high in all samples but particularly in tailing and sediment. In soil samples is particular high the Cd content. The comparison of obtained results with levels of risk estimation based on chemical mobile forms (table 1) (Barbafieri *et al.* 1996) show that in the soils near the contaminated site Zn and Cd are over the trigger limit, Pb is in less mobile forms even if are over the trigger limit. The levels of Zn, Pb and Cd are over the limit of Intervention in the case of tailings and sediment samples, as we expected.

Metals	Tailing	Sediment	Soil 1	Soil 2	Soil 3
Zn					
H_2O	+	+	*	*	-
KNO_3	-	+	-	-	-
EDTA	+	+	*	*	*
Pb					
H_2O	-	-	-	-	-
KNO_3	-	-	-	-	-
EDTA	+	+	*	*	+
Cd					
H_2O	-	+	-	-	-
KNO_3	+	+	-	+	-
EDTA	+	+	+	+	+

- Natural Values

* Trigger Limit

\+ Limit of Intervention

Table 1. Environmental impact assessment, based on heavy metal mobile species.

Metals accumulation by *Juncus compressus* in differents plant tissues

It is emerging a new remediation technology based on the use of metal accumulating plants to extract heavy metals from soil. Phytoremediation offers the advantage to be very cheep and non destructive of landscape. To increase the development of this process, it is fundamental to search plants with the ability to accumulate heavy metals and to growth in conditions particularly stress. *Juncus compressus*, of juncacee family, is able to growth on tailings and on sediments of this mine site (where heavy metals contents and bio-availability is very high) so it is considered a specie able to tolerate great contents of heavy metals. This plant show the ability to accumulate over 7000 mg/kg of Zn and 99 of Cd and 1600 of Pb in root. The metal accumulation decrease in rhizome (until 1600 of Zn, 117,5 of Cd and 112 of Pb), and in leaf is more low. Possibilities to use this plant in phytoremediation is under study.

Conclusion

This data confirmed that analysis on heavy metal mobile species (determined by sequential extraction procedure) is of great importance in order to evaluate the risk of heavy metals contamination. This region is not high populated so risks for human been could be limited, but the spread in the long term of these toxic elements in close areas, can increase the level of contamination compromising soil quality. In fact near the site are present areas under agricultural or pasture management and so it is fundamental to prevent the enter of this toxic substance in food chain.

Juncus compressus L., family of *Juncacee,* spontaneously grown on mine tailings, showed the ability to tolerate and accumulate very high concentration level presents in mine tailings so it could be a good candidate to employ in phytoremediation. Other plants species, grown in the close areas, will be analysed in the proceeding of the study.

References

Barbafieri M., Lubrano L. and Petruzzelli G. 1995. Chemical-remediation and Phytoremediation: effects on heavy metal mobility. *Fith International KfK/TNO Conference on Contaminated Soil, Maastricht*, pp.1141-1142.

Barbafieri M., Lubrano L., Petruzzelli G. 1996. Characterisation of pollution in sites contaminated by heavy metals: a proposal. *Annali di Chimica*.86:585-594.

Caboi R., Cidu R., Cristini A., Massoli-Novelli R., Zuddas P.1994. Water contamination in the mining area of Montevecchio (Sardinia). *In: Environmental Contamination. 6th International Conference*. Delphi, Greece :35-37.

DEVELOPMENT OF METHODS TO ASSESS POLLUTANT ATTENUATION IN GEOLOGICAL BARRIERS UNDER LANDFILL: OPTIMIZING PROCEDURES TO INVESTIGATE SORPTION; DIFFUSION AND COLLOID TRANSPORT

U. Förstner[1], J. Gerth[1], F. v.d.Kammer[1], L. Nordlohne[2], M. Silla[2] and R. Wienberg[2]

[1]Arbeitsbereich Umweltschutztechnik, Technische Universität Hamburg-Harburg, Eißendorfer Straße 40, D-21073 Hamburg;
[2]Büro und Labor Dr. R. Wienberg, Gotenstraße 4, D-20097 Hamburg

Keywords: adsorption, desorption, diffusion, dissolved organic carbon, nickel

SUMMARY

The Ihlenberg landfill near Lübeck is used as a model site to test and optimize methods for the characterization of the pollutant attenuation potential in geological barriers. The barrier consists of alternating layers of glaciofluvial sand, silt and till with different hydraulic conductivity, chemical reactivity and composition. With selected organic and inorganic pollutants batch sorption and diffusion experiments are conducted. Sorption studies are carried out according to the OECD guideline 106 (adsorption/desorption) with different pollutants and barrier materials in order to obtain sorption parameters for transport modeling. Diffusion is tested with non-disturbed and disturbed specimen after re-consolidation at pressures of 50 and 100 N/cm² which is equivalent to respective depths of about 25 and 50 meters. A stainless steel diffusion cylinder is filled with two non-contaminated segments forming a sandwich with a glass fibre filter as the source of either the conservative tracer (chloride) or the contaminant investigated (nickel and lindane) each tagged with the respective radioisotope ^{36}Cl, ^{63}Ni or ^{14}C labeled compound. After an appropriate diffusion time under pressure concentration profiles are obtained by dividing the segments into regular slices and measuring the activity in each slice.

It is the aim of the projekt to assess the role of colloids in the transport of pollutants. As a first step procedures are devised to characterize organic and mineral colloids by particle size separation using field flow fractionation (FFF). For the characterization of dissolved organic carbon a separation and detection system consisting of flow-FFF coupled with UV/VIS, fluorescence and laser light-scattering detectors has been developed. This system can be used to detect how the particle size of colloids is affected by changes in pH, redox potential and ionic strength. UV/VIS and fluorescence fractograms are recorded at different wavelengths and are compared. Particle sizes of natural colloids are calculated from laser light scattering data. Column experiments to study colloid formation in the Ihlenberg barrier material are carried out as a function of reaction conditions and composition of the solid. The mechanical transport of colloidal particles is tested under saturated conditions at different hydraulic conductivity, hydraulic gradient and colloidal size. First results indicate that dissolving carbonate is the major source of mineral colloids. Organic colloids in the waste leachate play a significant role in the transport of pollutants. The results on sorption/desorption, diffusion and the chemical and physical behaviour of colloids will be used as a basis to predict pollutant transport in the barrier.

This projekt is funded by the German Federal Ministry for Education, Science, Research and Technology (BMBF)

Investigation of *in situ* Remediation Alternatives for Soils Contaminated with High Sulphates and Heavy Metals

Indah R S Salami and G.K.Anderson

Research Assistant and Professor of Environmental Engineering
Department of Civil Engineering, University of Newcastle upon Tyne,
Claremont Road, Newcastle upon Tyne, NE1 7RU,U.K.

Keywords: contaminated soil, slurry, zinc, sulphate, case study

Background

An investigation was carried out on a 25 hectare site with an average depth of 15m, in Gateshead, U.K., which had been contaminated for over 100 years. The contamination has resulted from a wide range of wastes from industries such as chemicals factories, ship building and a gas works. Environmental problems from the area include sulphide gas affecting a nearby housing development and leachates containing high levels of sulphate discharging into the River Tyne. Much of the soil from the whole area contains high concentrations of sulphate and a wide range and varying concentrations of heavy metals.

Objective

The study was to investigate the treatability of the soil by *in situ* remediation, particularly related to sulphate and zinc concentrations. This was carried out using a soil slurry in a Warburg respirometer. Two separate and distinctly different soil samples (S1 and S2) were collected from the site. The remediation method proposed was to enhance the endogenous microbial activity after nutrient addition and adjustment of the soil environment.

Methodology

A slurry was made up consisting of dried soil and deionised water and was reacted with a series of nutrient mixtures, namely N and P, N only, P only and N and P plus some trace element sources and after homogenisation for 24 hours. Gas production and CO_2 evolution were compared between treatments along with pH changes and any residual concentration of contaminants. The study also involved glucose addition as an additional carbon source, acidification of the soil (pH adjustment), as well as both aerobic and anaerobic conditions of the reaction.

Results and discussions

In S1, the leachability of SO_4 was slightly higher in the aerobic headspace than for those in the absence of air. The highest sulphate concentration in S2 resulted from P addition. Statistically, the nutrient added and the availability of air affected the amount of zinc leached. With N & P, zinc was greatly reduced (70-86% in S1) whereas P only addition increased the zinc leachability in the soil (in S2). In this study, nutrient addition of 6mg N/l and 11mgP/l showed the greatest zinc reduction.

Mineralization of organic sulphur, which can occur both in aerobic and anaerobic conditions, depended on the availability of the carbon source. A carbon:sulphur ratio of 400:1 has been shown to result in immobilisation of S and at a ratio of 200:1 sulphur would be released into the environment (Paul & Clark, 1996; Killham, 1994). The test with a glucose addition of 2500µg/g (Wu *et.al.*, 1995) showed that additional glucose

increased CO_2 production. The further acidification of S2 gave a significant increase in CO_2 evolution. In addition, it also greatly increased the sulphate and zinc concentration in the leached supernatants. If immobilisation of S were the target, the system would require a higher quantity of the carbon source. Comparing the effects of the amount of glucose added to the system however, showed that the sulphate concentration did not reduce by the addition of glucose.

Table 1. Characteristics of soil samples

Parameters	Sample 1 (S1)	Sample 2 (S2)
pH ($CaCl_2$)	7.9	12.4
SO_4 (mg/kg dry soil)	4764	8944
Zn (mg/kg dry soil)	1294	2741
Organic matter (LOI, g/100g oven dry soil)	10	14
Organic nitrogen (mg/kg)	452	1205

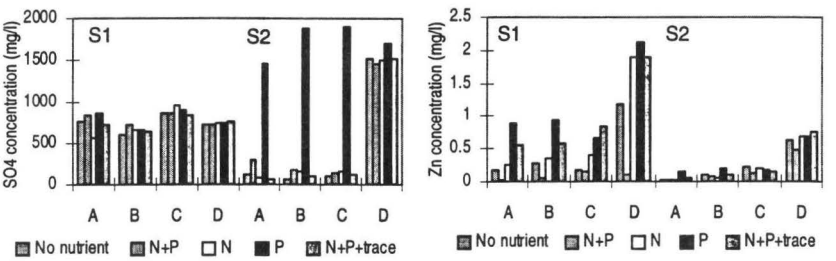


Fig.1 Sulphate and zinc concentrations after treatments
(A=aerob, B=anaerob, C=anaerob+glucose, D=anaerob+glucose+acidification)

It should be pointed out that acidification of soil with a high calcium content, could generate up to ten times more CO_2. Soil acidification would therefore need to be undertaken carefully in order to avoid misleading CO_2 values caused by chemical reactions rather than by microbial activity.

Conclusion

The study showed that in S1 the microbial activity was greater than in S2. Glucose and acidified soil produced higher quantities of CO_2. The least sulphate and zinc concentrations were obtained in the anaerobic system, whereas in S2 glucose and acidification generated a greater zinc concentration. Sulphate leached significantly with the addition of nutrients containing P in S2.

The slurry tests determined which soil conditions could not establish immobilisation of S while at the same demonstrating that zinc could be successfully removed. Further investigations in current and future soil treatments (such as homogenised or undisturbed soil columns, etc.) are being carried out to provide a more realistic response to the actual soil site conditions which may not be demonstrated by the reactions found in the slurry phase.

References

Killham, K. (1994) *Soil Ecology*, Cambridge University Press, Cambridge-Great Britain.

Paul, E.A., Clark, P.E. (1996) *Soil Microbiology & Biochemistry*, 2nd Ed., Academic Press, USA.

Wu, J., O'Donnell, A.G., Syers, J.K. (1995) Influences of glucose, nitrogen and plant residues on the immobilization of sulphate-S in soil, *Soil. Biol. & Biochem. 27, pp. 1363-1370.*

Consoil'98
Poster Presentation.
Theme C : Investigations, Characterisation, Behaviour & Fate of Contaminants

Contact: Dr. Jacqueline Anne Falkenberg
Nellemann, Nielsen & Rauschenberger A/S
Sortemosevej 2
DK-3450 Allerød
Denmark

Tel: (45) 48 14 00 66
Fax: (45) 48 14 00 33
e-mail: jaf@nnr.dk

Title: Sampling Strategies and Analysis of Soil Samples

Jacqueline Anne Falkenberg & Michael Mücke Jensen
Nellemann, Nielsen & Rauschenberger A/S & The Danish Environmental Protection Agency

New Draft Guidelines for Contaminated Soil

In connection with implementation of a revision in legislation on contaminated soils, the Danish Environmental Protection Agency is preparing a series of guidelines to cover aspects from the initial mapping and registration of contaminated sites, sampling and analysis, remediation as well as classification and reuse of contaminated soils. The guidelines on sampling and chemical analysis of soil samples are to be used in connection with site investigations and remedial projects.

Standardisation, Innovation and Optimisation

The purpose of the guidelines is to ensure a standard approach to sampling and analyse of soils samples, but at the same time allow room for innovation and optimisation. These somewhat contradictory objectives are achieved by defining rigorous requirements for documentation of the sampling and analyse.

Historical Site Information and Pollution Model

A detailed historical description of past activities and potential pollutants at the actual site is a requirement for the preparation of sampling and analytical strategies. Previous experience gained at similar sites and general information on the use of chemicals and geological/ hydrogeological conditions can be used to check and calibrate the pollution "model". The pollution "model" is merely a detailed description of the expected nature and distribution of pollutants.

Sampling Objectives

The sampling objectives need to be unambiguously defined and clearly depend on the objectives for the investigation. For example;

- The investigation shall determine the need for remediation with respect to end-use as a recreational area with lawns and flower beds - the sampling strategy concentrates on the critical pollutants in top soil around possible sources of pollution.

Contaminated Soil '98, Thomas Telford, London, 1998, 985–986

- The investigation shall determine compliance with soil quality criteria in soil due to atmospheric deposition of lead and PAH from traffic - a sampling strategy comprises a symmetrical net with analyses for lead and PAH .
- The investigation shall determine the nature and extent of soil contamination around former industrial installations. The objective is to assess whether a complete clean-up can be achieved or whether only partial clean-up and restrictions of end-use is more realistic economically. The sampling strategy needs to determine the chemical identity of the pollution, the extent of pollution in the boundaries for unpolluted and polluted soil including the depth of pollution

Unit Sampling Areas

On the basis of the historical information, a pollution "model" is defined. The future use of the site and identification of areas with particularly vulnerable end-use (e.g. housing projects) determine placement of unit sampling areas. These unit sampling areas can be of different size and have different sampling and analytical programs.

Economically and Statistically Realistic Objectives

In the absence of information on past practices, a very clear definition of the objectives of the investigation must be made. This is important in that no sampling strategy can find small isolated sources of pollution and realistic objectives need to be defined before the investigation is initiated.

Quality and Quality Assurance

All aspects such as:

- the assessment of past practices,
- the definition of the scope and objectives of the investigation,
- the risk assessment,
- the investigation strategy
- the initial planning of the location, depth and method to physically take soil samples
- the type of analyses performed on the samples,

affect the quality of the final result. The draft guidelines are therefore concerned with the need for documentation and quality assurance of the methods used for sampling and analysis. Furthermore justification for the choice of method as related to the objective and scope of the investigation is required.

CLASSIFICATION AND SOIL QUALITY MONITORING; A CASE STUDY

G. Mol, S.P. Vriend and P.F.M. van Gaans

Departments of Geochemistry and Physical Geography, Utrecht University, P.O.Box 80021, Utrecht, The Netherlands, e-mail: gmol@earth.ruu.nl, vriend@earth.ruu.nl, p.gaans@frw.ruu.nl

Key words: soil, monitoring, data analysis, spatial variability, sampling strategies

INTRODUCTION

Soil monitoring networks, both national and regional (provinces), are a recent addition to environmental monitoring activities in the Netherlands. The various provincial networks have been operational for a few years now and have produced much data. Recently we raised some *a priori* questions concerning a.o. the concept of homogeneous subregions, based on a critical analysis of the network designs (Mol et al., *in press*). The current paper is based on actual data from the soil monitoring network of the province of Friesland, year 1997. This dataset comprises a large number of attributes measured in samples of the litter layer and of soil and soil moisture from different soil horizons. Here we will focus on the soil samples from a depth of 0-10 cm, comparing *a priori* classification models with *a posteriori* models.

METHODOLOGY

For the collection of the soil samples Friesland was divided into 14 so called "homogeneous land types" on the basis of soil type and land use. Each occurrence of a specific soil type - land use combination was considered representative for the homogeneous land type as a whole. Each land type was sampled at a number of field locations (4, 10, or 20 depending on its relative total area). At each location four different land parcels close to each other were sampled, on every parcel one composite sample (of 40 subsamples) was collected. This sampling scheme resulted in a total of 472 samples, which were analysed for some 15 attributes, using standard techniques (see van Gaans et al., 1995).

Subsequent data analysis aimed at finding an optimal classification or regression model, that would describe most of the variation in the data with a minimum number of explaining variables. To this end, the statistical analysis comprised an analysis of the type of distribution of all attributes, a cluster analysis, several analyses of variance (ANOVA) using both the *a priori* land type classes and the *a posteriori* clusters, and a series of multiple linear regressions versus clay, organic matter, and $CaCO_3$ content.

RESULTS AND DISCUSSION

As most attributes showed lognormal characteristics, subsequent statistical techniques have been performed on logtransformed data. A cluster analysis, using clay, organic matter and calcite, led to an interpretable 5-cluster model (table 1). Cluster 1 and 2 are sandy soils respectively poor and rich in organic matter, cluster 3 is predominantly characterized by its $CaCO_3$ content, cluster 4 and 5 are respectively the peaty and clayey soils.

	Cluster 1	Cluster 2	Cluster 3	Cluster 4	Cluster 5
Clay	0.41	3.27	14.02	14.84	27.92
Organic matter	2.75	9.13	4.88	30.44	12.18
$CaCO_3$	0.07	0.15	2.25	0.42	0.41

Table 1. Cluster centres after Fuzzy *c*-means Clustering using Clay (%), Organic matter (%) and $CaCO_3$ content (%).

A hierarchical ANOVA, based on the original classification in 4 soil types, and 14 soil type-land use combinations was compared with a one-way ANOVA based on the clustering, and with the results of the multiple linear regressions (table 2). Because differences in land use are often largely related to differences in soil type, their influences could not be separated in a two-way ANOVA.

	4 soil types	14 land types	5 clusters	regression
As	72	74	58	64
Cd	16	32	27	34
Cr	65	79	74	84
Cu	39	76	61	59
Hg	18	55	36	40
Ni	72	78	72	80
Pb	20	51	49	60
Zn	55	80	72	81

Table 2. Percentage of variance explained by different classifications.

The inclusion of land use in addition to soil type in the model increases the percentage of explainded variance primarily for the "anthropogenic" elements: Cd, Cu, Hg, Pb, and to a lesser extent Zn. However, the 5-cluster *a posteriori* model performs almost equally well as the *a priori* 14 land type model, except for As. It certainly is an improvement over the *a priori* soil type classification. Being based on continuous rather than on nominal parameters, the regression model with only 3 explaining variables also appears adequate.

REFERENCES

Gaans, P.F.M. van, Vriend, S.P., Bleyerveld, S., Schrage G. and Vos A. (1995) Assessing environmental soil quality in rural areas. A base line study in the province of Zeeland, the Netherlands and reflections on soil monitoring network designs. *Environmental Monitoring and Assessment* **34**, 73-102.

Mol, G., Vriend, S.P. and van Gaans, P.F.M. (*in press*) Future trends, detectable by soil monitoring networks? *Journal of Geochemical Exploration*

Monitoring of Kerosene Infiltration in an Unsaturated Sandy Soil at Semifield Scale in the Wageningen Rhizolab

C.S. Hwu[1], J.T.C. Grotenhuis[1], G. Malina[1], A.L. Smit[2], and J. Groenwold[2]

[1]Subdepartment of Environmental Technology, Wageningen Agricultural University, P.O. Box 8129, 6700 EV Wageningen, and [2]DLO-Research Institute for Agrobiology and Soil Fertility (AB-DLO), P.O. Box 14, 6700 AA Wageningen, The Netherlands

keywords: monitoring, soil gas, in situ measurement techniques

Introduction

Kerosene, often used as aircraft fuel, is a complex hydrocarbon, containing immobile as well as more mobile components. Especially the mobile components in kerosene may threaten the quality of groundwater if a spill occurs. Therefore the transport of kerosene, especially the infiltration rate of its components, was studied on semifield scale (2.5 m^3) by *in situ* monitoring the soil gas with photoacoustic spectroscopy as well as gas chromatography (GC).

Experimental

In the AB-DLO facility Wageningen Rhizolab (van de Geijn et al., 1994), 3 compartments (dimensions: 1.25 m x 1.25 m x 1.65 m) were filled homogeneously with a sandy soil (4% organic matter, 10% (w/w) water (ca. 56% of field capacity)), at a bulk density of 1400 kg/m^3. To determine the composition of the soil gas (CH_4-equivalents) 48 gas sampling cells (2.5 cm Ø x 2.5 cm long) were placed in each compartment and were connected with air-tight viton tubing (Ø=1mm). Per layer of 10 cm the cells were placed at the centre, and at 25 and 50 cm from the centre of each compartment. Except for those in the centre the location of the sampling cells was at random.

Two compartments were contaminated with 3 l kerosene in the centre at a depth of 50 cm below the soil surface. The kerosene was infiltrated at an area of 64 cm^2 using a pressure head of about 5 cm, resulting in a constant flow rate of on average 0.085 l/h for the two compartments (0.092 and 0.076 l/h respectively).

Within 1 h a sampling program was started for the soil gas by using the CH_4 channel of a BK1311 apparatus (Brüel and Kjær, Denmark) for *in situ* measurement of kerosene (CH_4-equivalents) as well as directly thereafter for GC-analysis. Gas samples (100 µl) were stored for maximal 1.5 h in 1.2 ml gas-tight vials and were analysed with HP5890 series II GC (column: Chrompack cp-sil-5, 25 m x 0.53 mm; Temp.: inlet 280 °C, oven 170 °C, FID detector 300 °C; carrier gas: helium, 100 kPa at 11.4 ml/min).

Data of *in situ* monitoring by BK1311 and GC analyses were analysed using the surface mapping programme Surfer (Golden Software, Colorado, USA).

Results

The infiltration of the kerosene was followed with time in compartment 1 and 2 respectively for 6 and 8 days by soil gas analyses. Thereafter in compartment 1 bioventing was started, whereas in compartment 2 the same flow of air (600 l/h or ca. 400 $l/m^2/h$) was ventilating the headspace of ca. 200 l.

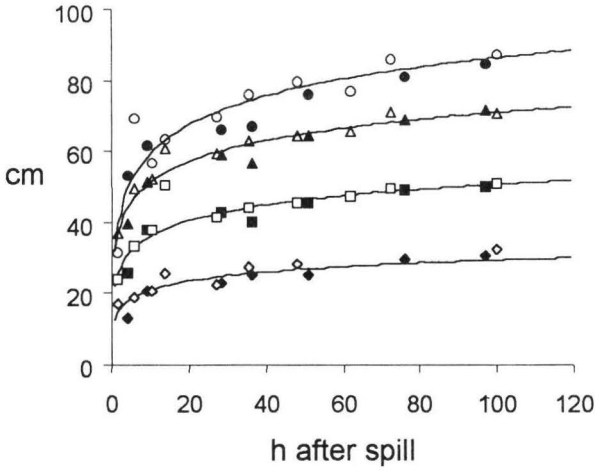


Figure 1: The relationship between the distance in cm (from the point of contamination in vertical downward (○ ●), vertical upward (◊ ♦), horizontal (□ ■) and diagonal downward (Δ ♦) direction) where a concentration of 0.1% CH_4-equivalents was reached versus time (h) after contamination. Closed symbols are for compartment 1, open symbols for compartment 2.

The iso-concentration lines of 0.1% CH_4-equivalents in time were used to illustrate the infiltration behaviour of kerosene. Figure 1 shows at which distance from the point of contamination (in four directions) this concentration was reached. The infiltration in vertical-downward direction was the highest, whereas that in vertical-upward direction was the low st. Data from compartment 1 (closed symbols) matched very well with data from compartment 2 (open symbols).
Regarding infiltration, the GC measurements confirmed the measurements by BK1311. However, GC analysis revealed a relative change in soil gas composition, as it contained relatively more lighter components like toluene and iso-octane at a larger distance from the source than heavier components like xylene and decane in all directions.

Conclusions

The infiltration distance with time of kerosene in two compartments measured by the CH_4 channel of BK1311 matched very well, therefore it can be concluded that the experiments performed with the semifield scale (2.5 m^3) facility in the Wageningen Rhizolab are quite well reproducible.
A relative increase in volatile low molecular weight components at increased distance with time could be demonstrated by GC analysis.

Literature

Geijn, S.C. van de, J. Vos, J. Groenwold, J. Goudriaan and P.A. Leffelaar (1994). The Wageningen Rhizolab – a facility to study soil-root-shoot-atmosphere interactions in crops. I. Description of the main functions. Plant and Soil 161, 275-287.

POTENTIALS AND BARRIERS OF HEAVY METALS BIOAVAILABILITY IN SOIL

P. Bielek[1]
[1] Soil Fertility Research Institute, Gagarinova 10, 827 13 Bratislava, Slovak Republic

Key words: heavy metals, bioavailability.

Heavy metals bioavailability in the soil belongs to the most actual subject of interest in science and in many kinds of other human activities. Not enough results and some gaps of knowledges in bioavailability and in heavy metals uptake by plants are motivating for many new research activities in all over the world. Thanks to the research project granted from Ministry of Agricultural we are able to present some results in this area.

In controlled condition of vegetation experiments were examined: influence of liming a different soil water capacity on Cd, Zn and Pb transport from soil into the maize and rape plants. Soil (Eutric Fluvisol) which was use in experiment was in site polluted (14,1 $mg.kg^{-1}$ Cd, 936 $mg.kg^{-1}$ Zn and 1 144 $mg.kg^{-1}$ Pb). It is over limits valid in Slovak Republic.

Higher uptake of heavy metals was determined in rape plants (shoots) than in maize. Liming contribution was not significant measure in heavy metals accumulation in plants (not even under higher dose). At higher soil moisture (90 % WHC) was decreased the uptake of Cd and Zn by both kind of plants (in comparison to 40 % WHC).

Heavy metals (Cd, Pb, Zn, Co, Cr, Cu, Ni) were determined in 119 different soil samples (taken up in polluted areas of Slovakia). Following soil extractions were carried out: 2M HNO_3; 0,05M EDTA; 1M NH_4NO_3; 0,01M $CaCl_2$; HF + HNO_3 + HCl.

FAAS or GAAS methods of determination were used. Also plant analyses (same sampling sites) were done with aim to have the data about heavy metals transports (Cd, Pb, Zn, Co, Cr, Cu, Ni) into the shoots (FAAS or GAAS methods of analyses were used).

Following extraction intensities were found out from experimental data (soil analyses): HNO_3 - Cd > Pb > Cu > Zn > Co > Ni > Cr; EDTA - Cd > Pb > Cu > Zn > Ni > Co > Cr; NH_4NO_3 - Cd > Zn > Ni > Cu > Pb > Co > Cr; $CaCl_2$ - Cd > Zn > Ni > Cu > Co > Cr > Pb. Significant correlations between soil pH and heavy metal contents were identified in case of NH_4NO_3 and $CaCl_2$ extractions. pH 6,5 - 7,5 was beginning of significant extraction. Highest levels of extraction were found out below pH 5,5.

Humus contents did not affect significantly extraction potentials of heavy metals from soils.

Correlations between soil and plant heavy metals contents were found out as follows: Cu (in case of NH_4NO_3 extraction), Pb (in case of EDTA extraction), Ni (in case of $CaCl_2$ and NH_4NO_3 extractions), Zn (in case of all extractions), Cr (in case of HNO_3 extraction), Cd (in case of all extractions), Co (no correlation).

Effect of fertilizers on heavy metals uptake by plant was determined in field conditions (Cd, Pb, Zn contaminated Eutric Fluvisol). Following variants of experiment were observed: no fertilized, 60N - 12P - 17K, 120N - 24P - 34K, 200N - 70P - 80K (NPK in $kg.ha^{-1}$). Oats (1996) and rye (1997) were cultivated.

Contaminated Soil '98, Thomas Telford, London, 1998, 991–992

Applied NPK fertilizers did not affect the heavy metals concentrations in plant tissues. Of course, higher yields in fertilized conditions led to higher heavy metals uptake (significant correlation).

Effects of reduced tillage system of farming was investigated on heavy metals (Cd, Zn, Pb) availability in the soil and heavy metals uptake by plants in same field conditions (Cd, Zn, Pb contaminated Eutric Fluvisol). When tillage was reduced higher contents of available heavy metals forms were determined in the soil (in comparison with conventional farming system).

INFLUENCE OF VARIABLE PORE WATER VELOCITY ON THE RETARDATION OF REACTIVE SOLUTES

P. Seuntjens[1], C. Cornelis[1], J. Nouwen[1], P. Geuzens[1], R.F. Verheyen[2]

[1] Flemish Institute of Technological Research, Boeretang 200, 2400 MOL, Belgium
[2] Department of Biology, University of Antwerp, Universiteitsplein 1C, 2610 WILRIJK, Belgium

Key words: transport modeling, unsaturated soil, functional layers, reactive solutes, cadmium

Introduction

Several factors and processes influence the transport and fate of dissolved chemicals in soils. Natural soils are known to exhibit a large variability in hydraulic and sorptive properties. These properties influence the flux through which reactive solutes will move towards the water table. Transport of reactive solutes through a porous medium is classically described by three parameters: the convective pore water velocity v, dispersion D and a retardation coefficient R. A massive amount of literature concerns the characterisation of spatially variant transport parameters for soils by means of non-reactive tracers (e.g. Butters and Jury, 1989; Ward et al., 1995). To a much lesser extent, attention has been paid to spatially variable sorptive properties on one hand and to the influence of variable pore water velocity on the retardation of reactive solutes on the other hand (e.g. van der Zee and van Riemsdijk, 1987; Destouni and Cvetkovic, 1991). The retardation factor is commonly calculated using results of static batch experiments. Major advantages of this method are simplicity and considerable time savings compared to column studies. However, column studies are believed to better reflect natural soil conditions. Large experimental times are major drawbacks. This paper describes the experimental setup for the derivation of solute transport parameters of layered podzol profiles.

Materials and Methods

Pedogenetic layers in three distinct profiles in a podzol toposequence near a zinc ore smelter are sampled using acrylic columns (10 cm long and 5.6 cm diameter). Four undisturbed replicates are taken in each layer. The columns are capped and transferred to the laboratory, where each column is fitted onto a glass porous plate. Before applying solute on top of the column, residing pore water is extracted for analysis of major ions and metals. Subsequently, columns are saturated from the bottom in order to create a stable wetting front. At the top of the column solute is added through a minicartridge peristaltic pump. The column is connected to a vacuum chamber, maintaining a unit hydraulic gradient throughout the column. In a first stage, a steady unsaturated flow of background electrolyte (0.002 M $CaCl_2$) is imposed to the column, followed by an injection of a pulse of a conservative tracer (0.01 M $CaCl_2$). During the experiment, electrical conductivity of the outcoming soil solution is monitored continuously. The procedure is repeated for four different flux densities (0.5; 1; 10 and 100 cm/d).

Contaminated Soil '98, Thomas Telford, London, 1998, 993–994

Depending on the considered soil layer and the experimental conditions (flow rate), an appropriate curve fitting model is selected for estimating transport parameters (e.g. Toride et al., 1995). The classical approach is to fit v and D using the convective dispersive equation, which assumes physical equilibrium conditions (homogeneous matrix flow). This approach is expected to be suitable for homogeneous structureless layers (C-horizon). For the humic upper layers, showing heterogeneous flow, the classical approach in general is not suitable and has to be replaced by models taking micro-heterogeneity into account. After injection of the conservative tracer a sorbing, but mobile tracer (cadmium) is added to the column and collected in a fraction collector. A preliminary characterisation (table 1) of the soil profiles reveals that under actual conditions cadmium is transported downwards with an average piston flow velocity of about 1 m per 25 year (using a flux of 1 mm/d).

Table 1: Estimation of actual contaminant (cadmium) velocity (v_C) through different pedogenetic layers (q = 36.5 cm/yr; θ = 0.2 $m^3.m^{-3}$; ρ = 1400 $kg.m^{-3}$; k^* = 0.05 $mg^{1-n}.l^n.kg^{-1}$; m = -0.5; n = 0.85). Data are mean values of 3 observations.

dry podzol				wet podzol			
Layer	Cd_T ($mg.kg^{-1}$)	k ($mg^{1-n}.l^n.kg^{-1}$)	v_C (cm/yr)	Layer	Cd_T ($mg.kg^{-1}$)	k ($mg^{1-n}.l^n.kg^{-1}$)	v_C (cm/yr)
O	6.8	50.4	0.4	O	5.5	37.0	0.6
A	1.6	7.6	3.3	A	1.9	9.4	2.7
E	1.2	3.6	7.1	E	1.4	3.5	9.7
Bh1	4.6	11.8	2.2	Bh1	2.1	7.4	3.5
Bh2	1.7	5.1	4.8	Bh2	1.1	6.1	4.6
BC	0.88	4.6	5.1	BC	0.70	2.9	8.7
C	0.67	1.7	14.6	II	0.74	2.6	9.7
Cg	0.60	1.5	18.4				

Again, the same four different flux densities (0.5; 1; 10 and 100 cm/d) are imposed. Using small column lengths and a $CaCl_2$ background electrolyte, and maintaining a pH between 3.5 and 4 during the transport experiments, breakthrough is observed in a few weeks. Parallel to the column experiments, batch tests using the same pH range and background electrolyte are carried out.

References

Butters, G.L., and W.A. Jury. 1989. Field scale transport of bromide in an unsaturated soil. 2. Dispersion modeling. Water Resour. Res. 25: 1583-1589.

Destouni, G. and V. Cvetkovic. 1991. Field scale mass arrival of sorptive solute into the groundwater. Water Resour. Res. 27: 1315-1325.

Toride, N., Leij, F.J., and M. Th. Van Genuchten. 1995. The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments. Version 2. U.S. Salinity Laboratory, USDA, Riverside California. Res. Report No. 137. 121 pp.

Van der Zee, SEATM, and W.H. van Riemsdijk. 1987. Transport of reactive solute in spatially variable soil systems. Water Resour. Res. 23: 2059-2069.

Ward, A.L., R.G. Kachanoski, A.P. von Bertoldi, and D.E. Elrick. 1995. Field and undisturbed column measurements for predicting transport in unsaturated layered soil. Soil Sci. Soc. Am. J., 59: 52-59.

AN IN-SITU BIOSTIMULATION STRATEGY FOR INTRACTABLE SHORELINE SEDIMENTS CONTAMINATED WITH DIESEL FUEL

Bernard J. Peasley[1] and Dr. Turlough F. Guerin[2]

[1] International Development Technologies Centre, University of Melbourne, c/- PO Box 827, Moonee Ponds, 3039, Australia; fax: + 61 3 9375 7489; email: kimpan@enternet.com.au

[2] Rio Tinto Research and Technology Development, 1 Research Avenue Bundoora, Victoria, 3083, Australia, fax: + 61 3 9242 3222, email: Turlough.Guerin@riotinto.com.au (main author)

KEYWORDS in-situ, marine, bioremediation, natural attenuation, diesel, biosurfactant

SUMMARY A rocky, intractable and highly heterogeneous, intertidal zone, required the application of a non-invasive sampling and clean-up strategy, for a diesel fuel spill in an Australian tropical marine environment. The slow rate of natural attenuation, combined with continuing re-contamination from an inaccessible source, is compared with successful, low cost, non-invasive, in-situ treatments, using biostimulation with biodegradable surfactant and soluble, and slow release nutrients.

BACKGROUND In mid-1994, diesel fuel was spilled at an earthmover refueling bay in a Western Australian port. The bay was constructed 8 m above sea level, on a rockfill, battered steeply to the high tide mark. Receding tides exposed 25 m of gently sloping, rocky intertidal zone. Initial clean-up removed fuel in surface soils, but remaining diesel percolated through the rockfill, down the grade of underlying bedrock, onto the shoreline and into the sea. For 1-2 months, oily sheens were observed after tides flushed inaccessible voids in the rockfill. Diesel was trapped in the rockfill, in small pools of NAPL and thin surface films. The rockfill's solid construction however, precluded excavation to prevent further pollution of the sea. Contaminated shoreline sediments comprised fine silts, fine and coarse sands, coral fragments, skeletal particles, shattered shells, pebbles and stones, overlain by rocks up to 1m in diameter. This intractable rock covering, strewn over the contaminated intertidal zone, resisted extraction of comprehensive borehole data, needed to define the hydrocarbon plume and impeded access for sampling and clean-up activities. No contamination concentrations were available from the time of the spill, but a highly variable areal distribution was observed at the surface, indicating preferential welling pathways through the complex geology.

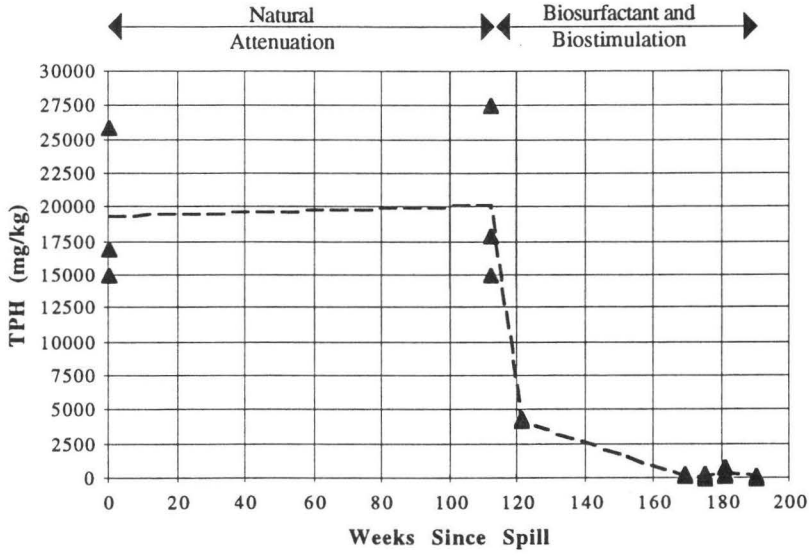
MATERIALS AND METHODS Sample analyses included pH, EC, available N&P, heterotrophic and hydrocarbon degrading microbial populations and the GC-MS and GC-FID analyses for TPH and biomarkers. Since contamination concentrations immediately after the spill were unknown, representative samples were saturated with diesel and free drained, to estimate 'diesel holding capacity' and hence maximum possible TPH concentrations at Week 0 (refer graph). C_{17}/Pristane and C_{18}/Phytane ratios were used to identify the extent of weathering and biodegradation, under the action of natural attenuation and throughout the treatment process.

SITE CHARACTERIZATION At Week 112, TPH concentrations at the high tide mark were 15,000–27,500 mg/kg and in the mid tide zone, 1,100–1,700 mg/kg. The mid tide zone may not have been contaminated to the same extent, due to the water level at the time of the spill, and this zone is also subjected to greater wave and tidal action. Assessment of the C_{17}/Pristane and C_{18}/Phytane ratio biomarkers, indicated that the contaminant had already begun weathering and that microbial degradation was occurring. TPH concentrations however, had not decreased over 112 weeks (refer graph), indicating fresh diesel was still being released from the rockfill into the high tide zone sediments. Total heterotrophes and total hydrocarbon degraders were found to be in the order of 10^4–10^5 orgs/g. Nutrient status was limiting, with < 3.4 mgN/kg and < 0.8 mgP/kg available. pH of sediments was generally between 8.5 and 9.2. EC varied markedly, with sediment particle size and type, in the range 1,100–5,000 µS/cm.

REMEDIATION STRATEGY A non-invasive clean-up strategy was designed to prevent further discharges to sea, remove residual diesel from the rockfill and to enhance

natural biodegradation processes, already present in the shoreline sediments. Biosurfactant and soluble N/P/K nutrient formula, were flushed into the rockfill via an agricultural drain at the spill site, to disperse and flush remaining diesel into shoreline sediments. A floating absorbent boom was used to prevent escape to sea, although no discharge was observed. Biosurfactant and soluble N/P/K nutrient formula were also sprayed over the rocks and sediments in the intertidal zone and slow release (5-6 mths) N/P granules were distributed to all accessible areas of sediment. Rockfill flushing was repeated at Weeks 121, 131, 177 and 183, with shoreline spraying and nutrient placement at Weeks 132, 173, 177 and 183. Treatments were interspersed with sampling and analyses to monitor progress.

RESULTS AND DISCUSSION The progress of remediation over 190 weeks since the spill, is represented in the graph below. The tri-phasic nature of the clean-up illustrates how the inherent slow rate of natural attenuation was improved by the relatively simple biostimulation strategy.



The dashed line joining the sampling means, shows the three rates of product removal. The second and most rapid stage was mostly due to dispersal at 170 mg/kg/day. To that point, natural attenuation was severely limited by the depleted nutrient status of the sediments and their near saturation with contaminant. It is believed the biosurfactant successfully dispersed the hydrocarbons more uniformly throughout the surrounding sediments, making them more available to the weathering action of the sea and intrinsic microbial populations, stimulated by greater nutrient availability. The third stage of 44 weeks, between Weeks 121 and 165, exhibited a removal rate of 12 mg/kg/day with no further treatments due to labour shortages. The activity between Weeks 165 and 190, featured further mobilization of diesel from the rockfill due to biosurfactant flushing.

After 69 weeks of treatment (44 of which featured no treatment activity), TPH concentrations reduced to 23–190 mg/kg, with many of the sampling sites reaching 'not detected' limits. Remaining hydrocarbons were within the C_{15}–C_{36} fraction. The total labour and materials cost for the clean-up of this 40 m^2 of shoreline, was in the order of AUD$13,000 and as such, this biostimulation strategy was a cost effective solution to what would otherwise have been a major disruption to the refueling bay and continuing marine pollution.

CHROMATOGRAPHIC MEASUREMENT OF ADSORPTION ISOTHERMS ON SOIL

S. Müller[1], H.G. Struppe[1], B. Ondruschka[1], M. Remmler[2], U. Roland[2], F.-D. Kopinke[2]

[1] Institut für Nichtklassische Chemie e.V., Permoserstrasse 15, D-04303 Leipzig
[2] UFZ – Umweltforschungszentrum Leipzig - Halle GmbH, Sektion Sanierungsforschung, Permoserstrasse 15, D-04303 Leipzig

Key words: adsorption, desorption, gas chromatography, naphthalene, soil, soil remediation

SUMMARY

During the development of a new method for the in-situ remediation of contaminated soils using radio-frequency (RF) energy, methodical studies in the laboratory and at the technical experimental plant scale have been carried out. In order to optimize the desorption process, knowledge about vapour sorption of organic contaminants in soils is necessary for the selection of suitable parameters and the evaluation of the success of the remediation process. Therefore, a method was developed, which allows the determination of sorption isotherms for volatile compounds in soils at high temperatures. The equipment used for this method consists of a modified gas chromatography system. The determinations were carried out using model soils such as pure sand and sand with a definite content of soil organic matter and clay.

KURZFASSUNG

Für die Entwicklung eines neuen Verfahrens zur in situ-Bodensanierung mit Hochfrequenzenergie werden gegenwärtig methodische Untersuchungen im Labor- und Technikumsmaßstab durchgeführt. Kenntnisse über die Gasphasensorption organischer Schadstoffe in Böden sind hierbei für die Auswahl von geeigneten Prozeßparametern und die Einschätzung des Sanierungserfolges unabdingbar. Deshalb wurde eine Methode entwickelt, die die Bestimmung von Sorptionsisothermen flüchtiger Verbindungen bei höheren Temperaturen erlaubt. Die hierfür verwendete Apparatur basiert auf Elementen der Gaschromatographie. Die Messungen erfolgten anhand von Modellböden, wie Sand bzw. Sand mit definierten Ton- und Huminstoffanteilen.

RÈSUMÈ

Dans le cadre de l'assainissement in-situ de sols grâce à l'énergie apportée par des ondes HF, des études comparatives au laboratoire et sur équipement de taille moyenne ont été menées. La connaissance de l'absorption des polluants organiques, contenus dans le sol, dans la vapeur d'eau est indispensable pour choisir les paramètres les mieux adaptés et évaluer le succès de ce procédé de décontamination. En outre, une méthode, qui permet de déterminer les isothermes d'absorption des composants volatils à haute température, a été développée. Le matériel utilisé pour cette méthode est constitué d'un système modifié de chromatographie en phase gazeuse. Les mesures ont été établies en utilisant des modèles comme de la silice pure ou en mélange avec une proportion bien définie d'argile ou des composés organiques.

Contaminated Soil '98, Thomas Telford, London, 1998, 997–998

Radio frequency (RF) heating is one method achieving in-situ decontamination of soil. The increase of the soil temperature due to the introduced RF energy leads to an enhanced desorption of pollutants either due to the increasing vapour pressure and diffusivity of the contaminants or due to strip effects. Investigations of the sorption and desorption equilibrium serve as a basis for the elaboration of new remediation techniques. In the course of such investigations the influence of parameters such as soil humidity, content of soil organic matter and content of clay are of particular importance.

Therefore, a method was developed, which allowes the determination of sorption isotherms of volatile compounds in soils in an elegant manner. The equipment used for this method consists of a modified gas chromatograph (DANI GC 1000), an environmental traces analyzer for automatic injection (DANI ETA 8521) and a chromatography data system (ESWE Gera, APEX 2.11). The kernel of the equipment is an empty HPLC column, which is filled with the soil to be characterized and installed in the GC oven. For the adsorption experiments a carrier gas flow of air containing a definite amount of analyte vapour is conducted over the soil sample. The enrichment of the air with the contaminant occurs in a separate thermostate.

The determination of the soil uptake is made by observing the concentration profile at the outlet of the column. For this purpose the ETA unit samples the outcoming carrier gas flow automatically after definite time intervals and injects this sample into a short capillary column, which is also placed in the GC oven. The adsorption and desorption of the analyte is recorded and analyzed by means of the chromatography data system over several hours. A 4-port valve makes it possible to realize the adsorption with dry air or air with a fixed relative humidity.

The determinations were carried out using model soils such as pure sand and sand with a definite content of soil organic matter and clay. Figure 1 shows, for example, the equilibrium isotherm of vapour sorption for the system naphthalene / sand determined at a temperature of 90°C. The isotherm is plotted as uptake vs. the relativ vapour concentration of naphthalene p/p_0.

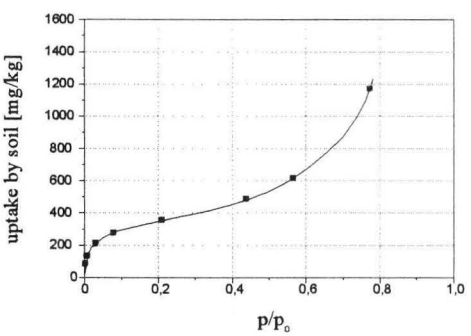


Figure 1: Sorption of naphthalene on sand at 90°C

The shape of the isotherm corresponds to the BET type-II adsorption, which is characteristic of vapour condensation to form multilayer adsorbates with nonspecific interactions. According to the BET equation, a molar heat of adsorption of 27.5 kJ/mol and a monolayer capacity of 270 mg/kg were calculated. The capacity is in good agreement with the monolayer capacity calculated from the specific surface area related to the size of the naphthalene molecule.

PHOTOACOUSTIC SPECTROSCOPY: AN ATTEMPT TO CHARACTERIZE SOILS AND SEDIMENTS CONTAMINATED BY PAHS

M.P. Cuypers[1], R. de Leeuw[1], O. Dóka[2], D. Bicanic[3], J.T.C. Grotenhuis[1] & W.H. Rulkens[1]

[1] Wageningen Agricultural University, Dept. Agr. Environ. Sys. Technol., Sub-dept. Environ. Technol., Bomenweg 2, 6703 HD Wageningen, The Netherlands.
[2] Pannon University of Agriculture, Dept. Physics, Mosonmagyaróvár, Hungary.
[3] Wageningen Agricultural University, Dept. Agr. Environ. Sys. Technol., Sub-dept. Agr. Eng. Physics, Wageningen, The Netherlands.

Keywords: characterisation, naphthalene, phenanthrene, photoacoustic spectroscopy

Introduction

In general, characterisation of PAH-contaminated soils and sediments focuses both on the contaminant and the sediment itself. Characterisation usually includes measurement of the contaminant concentration, the organic matter and carbonate contents, and the determination of particle size distribution. Sometimes, the distribution of organic matter and contaminants over the particle size classes is also determined. One parameter that, to our knowledge, is rarely considered is the physical state of PAHs. On the other hand, it is the physical state that may be a major factor in determining the clean-up possibilities for PAH-contaminated soils and sediments.

PAHs can exist in six basic physical states: as a particulate, as a liquid film, adsorbed to sediment particles, absorbed in organic matter, dissolved in pore water, and as a solid (or a liquid phase) in pores (Rulkens & Bruning 1995). No standard technique is yet available to determine the physical state of PAH contaminants. Here the potential of photoacoustic spectroscopy (PAS) for the determination of particulate PAHs is studied.

PAS is a linear spectroscopic technique that relies on the measurement of heat generated by the absorption of excitation energy by sample material. Following the absorption of excitation energy, the molecules relax by collisional de-excitation (in absence of luminescence, photo-chemistry, and photo-electricity). Such radiationless relaxation leads to the increase of kinetic energy and hence also to temperature rise. An increase of temperature within a cell of a fixed volume causes pressure increase, which is detected by a microphone, giving rise to a PA signal. In PA measurements, the wavelength of the excitation source is usually varied while maintaining other parameters unchanged. The PA spectrum contains information about the sample's optical and thermal properties.

This work concerns a PA study carried out on a model system comprising naphthalene, phenanthrene and glass-beads. Furthermore, the effect of particle size on the PA signal is investigated. The results indicate potential of PAS for gross estimation of the amount of PAH particulates in soils and sediments.

Experimental

PAS experiments were carried out in the UV-VIS part of the spectrum. Samples studied included naphthalene and phenanthrene crystals, glass-beads, and mixtures of: (1) glass-beads and naphthalene crystals (PAH concentration: 5, 10, 20, 50, and 75 % m/m), (2)

glass-beads and phenanthrene crystals (PAH concentration: 5, 10, 20, 50, 75 % m/m), (3) glass-beads, naphthalene crystals, and phenanthrene crystals (PAH concentration: 50 % m/m; naphthalene/phenanthrene ratio: 5/1, 1/1, and 1/5 m/m).
In order to study the effect of particle size on the magnitude of the PA signal, measurements were performed on powdered samples of naphthalene and phenanthrene.

Results
Naphthalene and phenanthrene exhibit a PA spectrum in the wave length range extending from 250-325 nm and 250-400 nm, respectively (absorption peaks at 305 nm and at 340 and 375 nm, respectively). In this range glass-beads are transparent and generate a negligible PA signal in the mixed model systems.
PA experiments with mixtures containing naphthalene/glass-beads and phenanthrene/glass-beads show larger PA-signals for increasing PAH concentrations. Regression analysis demonstrated a linear relation between the PA signal at 305 nm and the concentration of naphthalene; for phenanthrene a linear relation was found at 340 and 375 nm. For naphthalene r^2 is 0.93 at 305 nm, while in case of phenanthrene values of 0.83 and 0.84 were found for r^2 at 340 nm and 375 nm, respectively. The limit of detection (LOD) for naphthalene and phenanthrene in the model systems was 5 g/kg, which is much higher than the Dutch intervention value for PAH in soil (40 mg PAH per kg soil). However, the experiments with finely grinded PAH powders showed that LOD can be improved by increasing the area/volume ratio of the PAH particles. Therefore, knowledge on particle geometry is a must for quantitative determination of PAHs present in particles. Unfortunately, this information is generally not available for PAHs in soil and sediment systems.
Experiments with mixtures containing naphthalene, phenanthrene and glass-beads suggest the importance of phase for the interpretation of the PA signals. Due to different phases of two components in a mixture, the total PA signal (actually a sum of individual PA signals) might be zero despite the obvious presence of two PAHs.

Conclusions
Summarising, we conclude that at this stage PAS cannot be applied for the determination of PAH particulates in soils and sediments. The three main reasons for this are: (1) the high detection limit for coarse PAH particles, (2) insufficient knowledge on phase of individual PAHs, (3) the majority of PAHs exhibit fluorescence (which is a competing relaxation channel) and therefore low PA signals must be anticipated

References
Rulkens, W.H. & H. Bruning, 1995. Clean-up possibilities of contaminated soil by extraction and wet classification: effect of particle size, pollutant properties and physical state of the pollutants. In: Van den Brink, W.J., Bosman, R. & Arendt, F. (eds.), *Contaminated soil '95,* Kluwer Academic Publishers, Dordrecht, p.p. 761-773.

SCREENING OF GROUNDWATER TOXICITY DOWNGRADIENT OF A LANDFILL (GRINDSTED, DENMARK) USING A BIOTEST BATTERY

Anders Baun, Niels Nyholm, Poul L. Bjerg, and Thomas H. Christensen
Groundwater Research Centre/Department of Environmental Science and Engineering, Building 115, Technical University of Denmark, DK-2800 Lyngby, Denmark

Keywords: Bioassays, contaminated plume, hazard ranking, landfill leachate, organic contaminants, screening, toxicity

Introduction

Groundwater polluted with landfill leachate can contain a complex mixture of organic compounds for which traditional chemical analysis may not be sufficient for a hazard evaluation. Toxcity bioassays (biotests) carried out on polluted groundwater samples may provide a direct response that relates to the overall toxic properties of the compounds in the groundwater. In this paper a study of the toxicity of leachate-polluted groundwater downgradient of a landfill is presented. The study focused on assessing the toxicity of organic pollutants in the plume using solid phase extraction in combination with a battery of standardizedbiotests.

Materials and methods

Leachate polluted groundwater was collected from the anaerobic aquifer at Grindsted landfill (Denmark). The landfill has received mixed waste from the 1930s to the 1970s. The leachate plumes were thoroughly described by Bjerg *et al.* (1995) and Rügge *et al.* (1995). 27 groundwater samples were collected in the pollution plume from the landfill border to a distances of 254 m downgradient of the landfill. A reference sample was collected from a unpolluted part of the aquifer. Groundwater samples were extracted by means of solid phase extraction (SPE) using XAD-2 resin (Baun and Nyholm, 1996), removing the inorganic constituents and the major part of the bulk organic matter.

The toxicity of organic contaminants downgradient of the landfill was established in standardized short-term biotests using luminescent bacteria (*Vibrio fischeri*), algae (*Selenastrum capricornutum*) and crustaceans (*Daphnia magna*). Furthermore, samples were tested in the *umu*C-test for genotoxicity. The *umu*C-test is a modified Ames test using genetically engineered bacteria (*Salmonella typhimurium* TA1535/pSK1002) and provides a general non-specific response to DNA-damaging materials.

Results and discussion

The use of pre-concentration procedures made establishment of concentration-response relationships possible for all samples tested in the toxicity tests. The SPE-method was applied under field conditions at Grindsted landfill and problems of anaerobic sample storage was reduced using this approach. The pre-concentration technique has to be further improved for routine use, but SPE seems to be an useful tool for the assessment of the toxicity of organic pollutants in groundwater.

Contaminated Soil '98, Thomas Telford, London, 1998, 1001–1002

Toxicity was detected in samples downgradient of the landfill using the biotest battery. The TU_{20}-values shown in Figure 1 express the number of times a sample has to be diluted to give 20% effect in the toxicity tests. The most toxic samples were found close to the landfill and groundwater toxicity decreased as a function of the distance from the landfill (Figure 1). At a distance of 114 m downgradient of Grindsted landfill, the samples had reached toxicity level comparable to the reference sample.

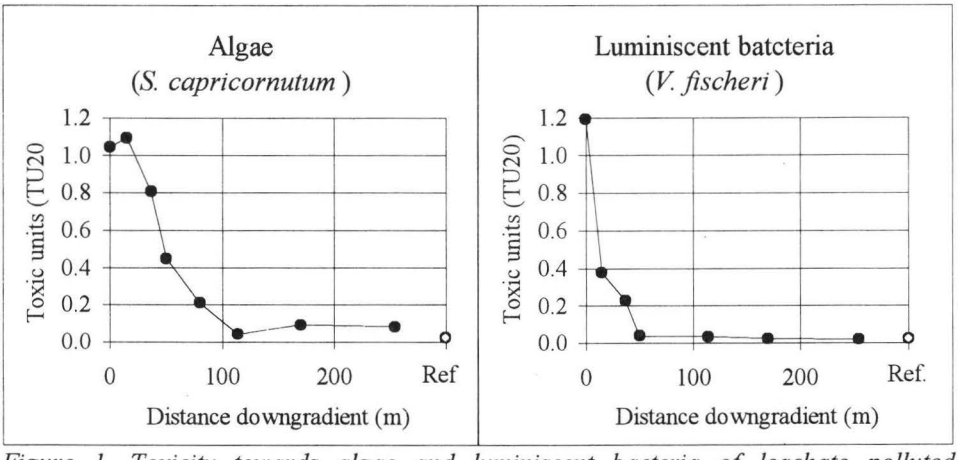


Figure 1. Toxicity towards algae and luminiscent bacteria of leachate polluted groundwater downgradient of Grindsted landfill. The samples were pre-concentrated by solid phase extraction (XAD-2). Ref.: Unpolluted reference sample.

A large variation in the sensitivity of the different biotests in the battery was observed. Algal tests (*S. capriornutum*) were more sensitive than tests with luminiscent bacteria (*V. fischeri*), whereas daphnia tests (*D. magna*) in general were insensitive to the constituents of the pre-concentrated samples. None of the tested samples showed genotoxicity in the *umuC*-test (*S. typhimurium*).

The results obtained in this study indicate that biotests applied on pre-concentrated groundwater samples potentially can be useful tools for toxicity characterization of organic chemical pollution in landfill-leachate polluted groundwater. For optimal performance, the bioassays testing should, however, be combined with chemical-analytical characterization.

References

Baun, A. and Nyholm, N. (1996). Monitoring Pesticides in Surface Water Using Bioassays on XAD-2 Pre-concentrated Samples.*Wat. Sci. Tech.*, **33**, 339-347.

Bjerg, P.L., Rügge, K., Pedersen, J.K., and Christensen, T.H. (1995). Distribution of Redox-Sensitive Groundwater Quality Parameters Downgradient of a Landfill (Grindsted, Denmark).*Environ. Sci. Technol.*, **29**, 1387-1394.

Rügge, K., Bjerg, P.L., and Christensen, T.H. (1995). Distribution of Organic Compounds from Municipal Solid Waste in the Groundwater Downgradient of a Landfill (Grindsted, Denmark).*Environ. Sci. Technol.*, **29**, 1395-1400.

Theme D:
Risk assessment, quality and health criteria

Estimation of occupational polycyclic aromatic hydrocarbons (PAH) exposure of employees at a contaminated site: comparison with the predictions of three exposure models

Frédéric DOR[1,2], Pascal EMPEREUR-BISSONNET[1], Denis ZMIROU[3], William DAB[1]

[1] EDF-GDF, Service des Etudes Médicales, 22-30 avenue de Wagram, 75382 PARIS Cedex 08,
[2] Agence de l'Environnement et de la Maîtrise de l'Energie, 27 rue Louis Vicat, 75015 PARIS,
[3] Université J. FOURIER (Grenoble), Laboratoire de Santé Publique, Domaine de la Merci, 38706 LA TRONCHE Cedex

Keywords : contaminated soil, exposure, 1-hydroxypyrene, PAHs, risk assessment, model.

INTRODUCTION

There are several thousand sites in France whose soil has been polluted by industrial activities. This heritage of a past that cared little about sustainable development leaves us today with serious management problems. Consideration of the health risks, among the factors that merit attention, has become essential, for it is now demanded by neighboring communities. This health risk assessment of contaminated soil raises many methodological problems. In particular, the accurate estimation of exposure levels of the populations living on or near polluted sites is a crucial step that largely determines the final results. This step is often performed using models that integrate all the exposure routes; the results of these models, however, often differ appreciably.

Our work has a double objective:

(i) to estimate the occupational exposure of workers on the sites of former gas factories by quantifying their urine levels of 1-hydroxypyrene (1-HOP), which reflect the total PAH,

(ii) to compare these results with those furnished by three different models (HESP, CLEA, AERIS).

MATERIAL AND METHODS

This study concerned hundred and ten persons who worked full-time at the contaminated site. Forty-six controls were also included in the protocol. The main exclusion criterion was current active smoking. The subjects formed three distinct groups according to their anticipated exposure level, based on their onsite activity. During one work week, we measured 1-HOP twice daily, at the beginning and end of each work day. At the same time, participants were equipped with devices for measuring exposure to respirable suspended particles (PM10), the PAHs content of which will be characterized. The design of the device, with two parallel sampling pumps, allows us to ascertain the relative proportions of occupational and nonoccupational exposure. In addition, from answers to a questionnaire, we were able to identify other confounding or interfering HAP sources, such as food, home location, and commuting method.

Contaminated Soil '98, Thomas Telford, London, 1998, 1005–1006

RESULTS

1) Comparison of the exposure dose estimates according to each model

Three multimedia exposure models were used for this comparison: CLEA (English), AERIS (Canadian), and HESP (Dutch). A simulation, based upon a fictitious situation and a standardized exposure scenario, was performed, taking into account the specific characteristics of each model. The results provided estimates that varied by several orders of magnitude (Table I). Moreover, the respective contribution of the different routes of exposure showed substantial disparities between the models. These differences arose from characteristics in the habitat, eating habits, and population, all of which had been defined for the country where the model was devised. The mathematical equations that modeled the transport and exposure phenomena were the other explanation.

Table I: Total exposure calculated by the three models for standardized scenarios:

A Residential

	HESP		AERIS		CLEA	
	Adult	Child	Adult	Child	Adult	Child
Benzo(a)pyrene	$3.9\ 10^{-3}$	$1.4\ 10^{-2}$	$8.5\ 10^{-4}$	$3.4\ 10^{-3}$	$1.4\ 10^{-3}$	$1.3\ 10^{-3}$
Cadmium	$5.5\ 10^{-5}$	$1.5\ 10^{-4}$	$4.6\ 10^{-5}$	$1.1\ 10^{-4}$	$4.3\ 10^{-3}$	$5.7\ 10^{-3}$
Benzene	$3.1\ 10^{-2}$	$8.2\ 10^{-2}$	$4\ 10^{-3}$	$8.9\ 10^{-3}$	$1.6\ 10^{-4}$	$6.4\ 10^{-2}$

Total doses are expressed in mg/kg of body weight per day

B Industrial

	HESP	AERIS	CLEA
	Adult	Adult	Adult
Benzo(a)pyrene	$6.9\ 10^{-4}$	$1.7\ 10^{-6}$	$1.7\ 10^{-4}$
Cadmium	$2.7\ 10^{-6}$	$7.6\ 10^{-9}$	$4.5\ 10^{-3}$
Benzene	$1.3\ 10^{-2}$	$6.5\ 10^{-4}$	$1.4\ 10^{-3}$

Total doses are expressed in mg/kg of body weight per day

2) Exposure measurements (1-HOP)

Data collection is done now and are analysing at this time. They will be presented at the conference. From the data analysis we will be able to: i) compare the urine concentrations of the biomarker according to anticipated occupational exposure, with analysis of variance between the three categories of employees, followed by a linear multiple regression; ii) evaluate the proportion of exposure attributable to onsite presence, in relation to overall exposure, especially atmospheric; and iii) compare the actual urine levels with those predicted by the models described above, after modeling the study situation. This comparison will furnish elements for validating the three models under study.

TIME-LABELLING SOIL REMEDIATION BASED ON ENVIRONMENTAL AND SOCIAL-ECONOMIC CRITERIA

C.A. Beurmanjer and C. de Boer

Department of Soil Remediation, Province of Gelderland,
P.O.Box 9090, 6800 GX Arnhem, The Netherlands

Risk Management and Health

Introduction

According to the Soil Protection Law in the Netherlands the responsible authorities (provinces and the major cities) must determine a year in which the remediation of a seriously contaminated site shall begin.
The large number of sites with serious soil contamination and the limited resources (financial, human, technical) makes it nessescary to assess priorities. A distinction is made between "urgent" and "non-urgent" cases of serious soil pollution. The difference between the two is based on the difference in risk of pollution to human beings, the ecosystem and in the annual increase of the amount of groundwater contaminated above the intervention value.
In urgent cases a year is determined (time labelling) by the authorities in which the remediation has to start. Recently a system has been developed for eshtablishing the year in which the remediation must begin. The year in which the remediation is to begin is based on environmental as well as on social-economic criteria.

Labelling the year of commencement soil remediation

General

To appoint the time to start the remediation takes place in two steps:
- division in three categories (table 1) on the basis of environmental criteria (actual human exposure, actual ecological exposure, actual diffusion in groundwater);
- appointing (labelling) the year to start the soil remediation within the categorie on bases of social economic-criteria.

Table 1: Classification based on environmental criteria

Category	Start remediation
I	$\leq$ 4 years
II	> 4 - $\leq$ 10 years
III	> 10 years - < 2015

This means that with all seriously contaminated sites, remediation must commence before 2015 (National Environmental Policy Plan 2).
The social-economic criteria enable authorities or others to make allowance for local and regional developments.

Contaminated Soil '98, Thomas Telford, London, 1998, 1007–1008

Environmental criteria

After investigation of the site, a risk evaluation is drown up to asses whether there is actual human exposure to the contaminants. This is done by a selection of all actual exposure routes (growing of crops, ingestion by children, inhalation of volatile subtances, etc). If the maximum permissible risk level is exceeded, remediation must start within 4 years (category 1). If the maximum permissible risk level is not exceeded, the site is not urgent in terms of human exposure.

Whether the contaminated site is "urgent" or "non-urgent" with regard to ecological exposure depends on whether of the HC50 (hazardous concentration) is exceeded and the contaminated surface.

In case of an urgent seriously contaminated site, the location will be classified in category I, if it is situated in an "ecological or natural scientific" valuable area. If not, the location will be classified in category II.

The risk of diffusion is estimated on the basis of two criteria:

- the annual increase in volume (table 2);
- the number of years to reach a vulnerable object (table 3).

Table 2: Classification based on increase in volume

Annual volume increase (m^3/y) above Intervention-value	Volume score: remediation appointed in
$\geq$ 5000	category I
$\geq$ 1000 and $\leq$ 5000	category II
$\geq$ 100 and $\leq$ 1000	category III

Table 3: Classification on time reaching a vulnerable object

One or more vulnerable objects reached within	Object score: remediation appointed in
0 - 4 years	category I
5 - 10 years	category II
11 - 20 years	category III

Social-economic criteria

In establishing when remediation will commence, within the category, social-economic criteria are taken into consideration. The following criteria can play a role:

- financial and business economic matters
- autonomic business and/or area development
- supplementary environmental criteria
- current technology
- social considerations

It is conceiveble that these criteria differ from place to place. In urban areas other criteria have priority than in rural areas. The authorities responsible can therefore fill in these criteria, to place policy emphasis at local and regional level.

References

- Hardeveld, W. van et al (1995) Soil and sustainebility: Dutch policy. Brink et al (eds) Contaminated Soil '95. Kluwer Academic Publishers, pp 1605-1618
- National Environmental Policy Plan 2, Lower House of Parliament, Session 1993-1994, 23 560
- Ministerie VROM, 18 februari 1997, Circulaire bepaling saneringstijdstip voor gevallen waarvoor sanering urgent is (in Dutch)

RISK ASSESSMENTS ON INDUSTRIAL SITES AS A POLLUTION PREVENTION METHOD - THE VIEW OF AN INSURANCE COMPANY

Martin Gawlik

UMB GmbH/R+V Insurance, J.F. Kennedystraße 1, 65189 Wiesbaden, Germany

Key words: chlorinated hydrocarbons, contaminated sites, environmental risks, hydrocarbons, laws, liability, risk, risk assessment, risk management, volatile organic compounds

1. Introduction

During the last 15 years about 130.000 contaminated sites have been identified and investigated in Germany. Most of them contain hazardous substances like hydrocarbons, volatile organic chlorines, policyclic organic matter, heavy metals and radioactive substances. Due to this situation an amount of 4 Billion DM had been spent by German insurance companies for the clean up of contaminated sites by 1995. This fact led the insurance companies to seek new guidelines for minimizing environmental risk exposures. The result was a new Environmental Impairment Liability Insurance with several differences in comparison to prior coverages and risk assessments for pollution prevention on customers´industrial and agricultural sites.

2. German Environmental Laws

The environmental law in Germany always consisted of federal and state laws and administrative rules and regulations. Among all environmental laws the most important issues for companies are the following:
- Federal Pollution Contol Act (Bundesimmissionsschutzgesetz [BImSchG])
- Waste Disposal Act (Kreislaufwirtschafts- und Abfallgesetz [Krw-/AbfG])
- Federal Water Management (Wasserhaushaltsgesetz [WHG])
- Federal Environmental Liability Act (Umwelthaftungsgesetz [UmweltHG])

3. Risk assessments, environmental management audits and liability assessments

Pollution prevention in the industrial sector has grown during the last years to a management priority. Pollution prevention means source reduction. To reduce or eliminate pollution sources, they first must be found and defined. Risk assessments, environmental management systems and liability assessments are important instruments for finding environmental risks and handling them in conformity with the valid laws.

Contaminated Soil '98, Thomas Telford, London, 1998, 1009–1010

The following diagram shows the way from risk assessment to risk management.

What are the benefits of pollution prevention?

The most important benefits are:
- reduced risk of liability
- cost savings
- improved company image
- public health and environmental benefits

4. Resume

The R+V's strategy of loss prevention. a combination between the new Environmental Impairment Liability Insurance Model. environmental risk assessments and environmental management systems (EC- Eco Audit as well as the ISO 14.000) offered by the UMB GmbH. shows good effects in loss prevention. The R+V Insurance Company noticed an evident decrease in the number of loss cases in assotiation with the increasing number of customers with installed risk management systems.

A MODEL RISK ASSESSMENT PROCEDURE FOR CONTAMINATED LAND

Dr. M.R. Harris

Monitor Environmental Consultants, 400 Aldridge Road, Great Barr, Birmingham, B44 8BH, UK.

Key words : Management, quality assurance, quality control, risk assessment

BACKGROUND

Assessing the risks that contaminated land may pose to health and the environment typically requires consideration of a wide range of complex technical issues. However, the technical process is rarely carried out in isolation or without reference to specific commercial, legal and financial factors.

If the technical process of risk assessment is to be successful, it has to be consistent, objective, transparent and have a proper regard for both the sources and effects of uncertainty on the decision-making process. If risk assessment is to find widespread practical application, it has to address the specific needs of a variety of different parties working in a variety of different contexts.

Standardised or "model" procedures offer one means of meeting the technical requirements of risk assessment while ensuring that its non-technical dimensions are taken into account.

OBJECTIVES OF THE PROCEDURE

A model procedure for risk assessment has been developed under the research programme on contaminated land managed by the UK Department of the Environment, Transport and the Regions. The procedure is one of a series of model procedures being developed by the Department and the Environment Agency, which address the whole process of assessing and managing the risks that may be associated with contaminated land (Herbert *et al*, 1995) [see also abstract by M.V. Smith to Theme E of this Conference]. The objectives of the model procedures are to:

1. Consolidate existing UK approaches into a structured but flexible framework.
2. Provide the criteria and supporting advice needed to ensure consistent, objective and transparent decision-making that has a proper regard for uncertainty.
3. Encourage and improve consistency in approach, terminology and understanding.
4. Provide a reference point for non-technical professionals who have to rely on the technical advice provided by others.
5. Improve the confidence of all those involved in the management of contaminated land.

Contaminated Soil '98, Thomas Telford, London, 1998, 1011–1012

The model procedures are not intended to be prescriptive, nor are they mandatory. However they are intended to provide a basis upon which individual users can build their own systems and approaches to suit their own particular needs.

STRUCTURE AND SCOPE OF THE PROCEDURE

The model procedure for risk assessment describes the objectives, scope, steps to be followed and expected outputs of each of a number of stages within risk assessment. Decision criteria are provided as an aid to decision-making at key points. Guidance is given on minimum information requirements for each stage of risk assessment, together with advice on the balance that has to be struck between the level of confidence required to avoid unwanted outcomes, and the cost of achieving that level of confidence. The procedure can be applied to a range of common contaminants and a variety of potential receptors, including humans, the water environment, flora and fauna and building materials.

The procedure also provides a framework for the practical application of specific risk assessment tools, including those developed through related Departmental or Agency funded research projects. These include the Contaminated Land Exposure Assessment (CLEA) model for the assessment of chronic human health risks [see Birstingl, J. and Ferguson, C., these proceedings] and Environment Agency methodology for assessing the impact of contaminated soils on the water environment (Environment Agency, 1996).

The poster provides more detailed information on the structure and scope of the model procedure for risk assessment, and describes how its various attributes can be applied for practical risk assessment purposes at an operational level.

Acknowledgement

The work described in this poster paper was funded by the UK Department of the Environment, Transport and the Regions (DETR). The views expressed are those of the author and not necessarily those of the DETR/Environment Agency.

References

Herbert, S. M., Harris, M. R. and Denner, J., *UK standard procedures for contaminated land,* in : Contaminated Soil '95, ed. Van den Brink, W.J., Bosman, R. and Arendt, F., Kluwer Academic Publishers, 1995

Environment Agency, *Methodology to determine the degree of soils clean-up required to protect water resources,* R & D Technical Report P13, Environment Agency Bristol, 1996

MAPPING THE RISKS TO HUMAN HEALTH FROM URBAN SOILS USING GEOSTATISTICAL TECHNIQUES

C P Nathanail[1], C C Ferguson[1], M J Browne[2], P J Hooker[2]

[1] Centre for Research into the Built Environment (CRBE), Nottingham Trent University, Nottingham NG1 4BU, UK. crbe@crbe.co.uk

[2] British Geological Survey (BGS), Keyworth, Nottingham

Key words: background levels; conditional simulation; geostatistics; human health risk; lead; mapping; risk assessment; spatial variability

As part of its Urban Environmental Survey of Wolverhampton, BGS commissioned CRBE to carry out a risk mapping exercise using geochemical data supplied by BGS[1].

An initial data analysis and variography of several Potentially Harmful Elements (PHE) established the feasibility of using geostatistical, or indeed any, interpolation techniques. This demonstrated that the PHE in the Wolverhampton dataset were spatially correlated, though with very large components of either small scale variability or measurement uncertainty (nugget effect).

The guideline values in common use at present in the UK, produced by the DoE Interdepartmental Committee for the Redevelopment of Contaminated Land (ICRCL), have been found to be inadequate and their scientific basis unclear. New guideline values are in the process of being derived using the probabilistic Contaminated Land Exposure Assessment (CLEA) model[3].

The study focused on a full geostatistical assessment of lead. The major sources of lead pollution in the environment are exhaust emissions from petrol vehicles, flaking of Pb-based paints, contamination of food and water from lead pipes and soldered joints, mining and smelting activities, former use of lead arsenate pesticides and application of sewage sludge to agricultural soils. Because of low solubility and resistance to microbial degradation, lead accumulates in the surface horizons in soil. The toxic effects of Pb have been extensively documented in both laboratory animals and humans. Lead is a general metabolic poison that affects many organs and organ systems.

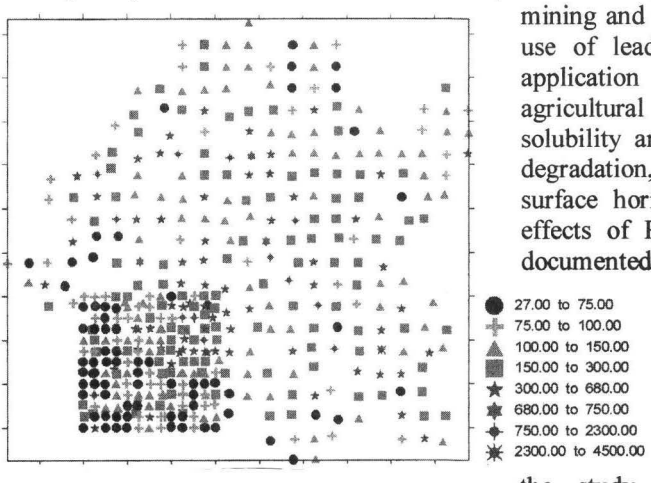


Fig. 1: Post plot of lead concentration (ppm)

Geostatistics involves the study of spatial phenomena[2]. Spatial correlation is quantified using the variogram. A best estimate of the most likely value is obtained using the weighted average techniques of kriging. If the probability of exceeding threshold values is desired then conditional simulation are used instead.

Contaminated Soil '98, Thomas Telford, London, 1998, 1013–1014

The BGS analysed 285 samples of soil on a 500 m grid and a further 169 samples on a 200 m grid (Fig 1). Variography showed lead concentrations to be spatially correlated and therefore spatial interpolation is valid. Since this is the basis for interpreting all site investigation findings and very few even consider the possibility that the soils at a site may not be spatially correlated, this is a particularly significant finding.

Measured concentrations of lead were compared with acceptable concentrations derived from CLEA. Conditional simulations have shown that there is a significant possibility of an unacceptable risk to human health from lead in urban soil. The probability of guideline values for residential areas with gardens being exceeded is between 4 and 6% for much of the study area. Conditional simulations offer a more powerful technique than kriging or other smoothing interpolators such as inverse distance, linear or triangulation (most commonly used in interpreting site investigation findings). Significantly, other interpolators may significantly underestimate the risk posed by a site where only some of the measured soil concentrations exceed the guideline value.

This geostatistical analysis represents several important developments in the approach to managing potentially contaminated land in the UK. For the first time, the spatial correlation of PHE in urban soils has been investigated and demonstrated. The large nugget effect reduces the effectiveness of commonly used interpolation methods used in interpreting the findings of site investigations.

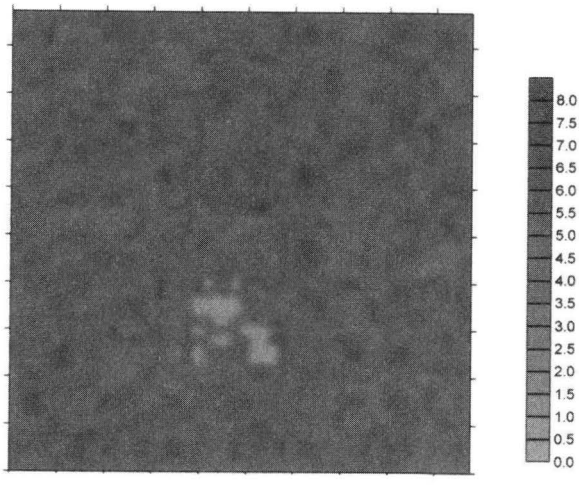


Fig 2 Lead Risk Map for Residential Land Use (Probability of exceeding guideline value)

Also for the first time, conditional simulation has been used to derive a map showing risk to human health from lead, assuming residential areas with gardens (Fig 2). The risk varies with land use and further work will determine the risks for non residential uses. The map shows that surface soils have elevated lead concentrations that would warrant further study to determine bioavailability.

The study should be used to inform the design of site specific risk assessments and should not be used in place of such assessments.

REFERENCES

1. BRIDGE ET AL. 1997. *Urban Environmental Survey of Wolverhampton.* British Geological Survey, Keyworth.
2. DEUTSCH C V & JOURNEL A G. 1993. *GSLIB: Geostatistical Software Library and User's Guide.* Oxford University Press, New York (2nd edition now published).
3. FERGUSON, C.C. (in press) *Guideline values for lead (Pb) contamination in soils.* CLR No. xx, Department of the Environment Transport and the Regions, London.

DEVELOPMENT OF A RAPID METHOD FOR IDENTIFICATION OF PATHOGENIC MICROORGANISMS BY THE POLYMERASE CHAIN REACTION (PCR)

H. Theißen[1] and U. Schies[2]

[1] IMAGO GbR, Schwedter Str. 34 a, D-10435 Berlin, Germany
[2] Tiefbau-Berufsgenossenschaft, TAD, Landsberger Str. 309, 80687 München, Germany

Key words: microorganism, analytical method, prevention, risk-assesment

Microorganisms pose a potential risk in many areas of waste treatment, rendering of industrial buildings or reconstruction of sewage drains. The identification of pathogenic microoganisms by classical methods are time consuming and prone to errors by false negative findings due to the methodology of phenotypic analysis. During the last few years, fast and reliable techniques for a genotypic analysis, namely the Polymersase Chain Reaction (PCR), have been established and used for identification and characterisation of microbial species and communities. Although several distinct protocols for isolation of bacterial DNA from soil and water, followed by genotypic analysis using PCR, have been published, up to now standardized methods do not exist. In order to improve the risk assesment of biological hazards, a set of standardized protocols will be developed for a fast and reliable identification of pathogenic microorganisms by using species-specific gene probes.
The overall development process will be dived in four steps:

1. Selection of species-specific oligonukleotid gene probes (primers).
2. Development of an optimized PCR-protocol in order to adress the special problem of identifying a few pathogenic microorganisms against a large background of nonpathogenics.
3. Development of a fast and easy procedure for quantitative detection of PCR-products
4. Development of procedures for isolation of microbial DNA, adopted for different sources like water, soil or air.

Each step of the development process can be carried out independendly from the others. This type of organisation simplifies the overall development process by compartimentizing the problems connected with the separate steps. A further advantage is the ability to expand the range of identifiable species or analysable sources by adding modified protocols to the corresponding level. Thus it possible to fit to different demands without loosing the overall uniformity.

BULK WASTE MANAGEMENT AND RISK ASSESSMENT FOR LARGE INFRASTRUCTURE PROJECTS

B. Guillaume, N.J. O'Riordan and A. Phear
Ove Arup & Partners, 13 Fitzroy Street, London, W1P 6BQ, United Kingdom

Keywords: sustainability, waste minimisation, risk assessment, regulations, data analysis

Constraints on land use often force the routes of infrastructure projects such as roads and railways onto marginal, low value land that may be contaminated. The creation of cuttings and excavations for these projects may thus result in contaminated materials as well as materials that can be potentially re-used. Environmental pressures, relating mostly to noise and visual intrusion often result in a lower alignment than would be required to maintain a balance of cut and "structural" fill materials, and also in the need for landscaped mitigation fills. Sustainable and environmental best practice is for waste to be minimised in the earthworks. The aim is thus to achieve, as far as practicable, a balance of cut and "structural" plus mitigation fill. This requires special considerations, which include:

- identifying appropriate re-use for spoil with low levels of contamination. This requires a risk assessment approach and may involve measures to control contamination migration.
- restoration of areas previously used for waste disposal affected by the development, including the restoration of containment measures.
- identifying appropriate means of management for surplus spoil which minimise adverse environmental impacts.

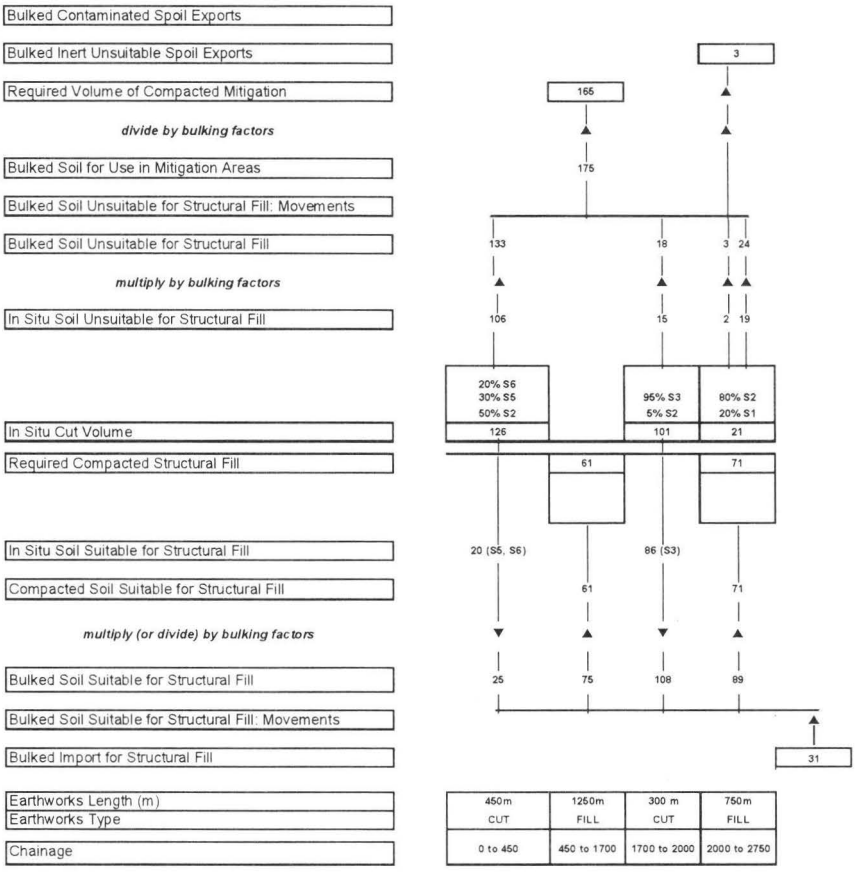
Activities undertaken must comply with legislation and in particular with waste management regulations and planning requirements.

The approach taken within Ove Arup and Partners begins with desk studies and then ground investigations, which address both engineering properties of materials and levels of contamination, followed by ongoing baseline monitoring. The investigations into ground contamination aim to fulfil data requirements to carry out risk assessments of soils in situ and determine waste management requirements for excavated soils. Risk assessments are undertaken to determine remedial action which may be required to prevent pollution incidents and risk to vulnerable receptors during and after construction.

In the design of infrastructure projects, estimates are made of the quantities of material required for "structural" embankments and "mitigation" fills and also of the quantities for various types of material arising from cuttings, excavations and tunnels. An example of a working earthworks movement diagram is given in Figure 1. These estimates include classifications of materials according to suitability for end use, based primarily on engineering properties. Material surplus to these requirements is made available to third parties or, as a last resort, disposed of as waste. In the UK, this enables Landfill Tax exposure to be calculated, in addition to the cost of excavation, haulage and disposal at the licensed tip.

Contaminated Soil '98, Thomas Telford, London, 1998, 1017–1018

To conclude, on large infrastructure projects, sustainable and environmental best practice is for waste to be minimised in the earthworks design coupled with risk assessment methods for assessing the suitability for reuse of material with low levels of contamination. In the UK, environmental legislation and taxation has recently been introduced to encourage sustainable practices in the construction industry.



Quantities in m^3 x 1000

Key

S1 - Made Ground; S2 - Head; S3 - Sand; S4 - High plasticity overconsolidated clay

S5 - Sands, silts and clays; S6 - Calcareous sandstones

Figure 1: Extract from a Typical Earthworks Movement Diagram

AN INNOVATIVE DECISION SUPPORT SYSTEM FOR QUANTITATIVE RISK ASSESSMENT AND CLEAN-UP OBJECTIVES SELECTION

Viet-Long DUONG[1], Pascal FORMISYN[1], Jacques BOURGOIS[1], Richard MODOLO[2]
[1]Department of Environmental Engineering, SIMADE Centre, School of Mines of Saint-Etienne 158 Cours Fauriel, 42023 Saint-Etienne, France Cedex 02
[2]GÉOCLEAN S.A., 5 rue Pascal, BP 170, 69686 Chassieu, France Cedex

Key words : databases, human health risk, exposure model, hazard ranking, guidelines, protection public safety

SUMMARY

The **TRACES** software (**T**ool for **R**isk **A**ssessment from **C**hemical **E**xposure to **S**oils) is an innovative fully integrated software for assessing hazard and risk levels of potentially contaminated sites.
It was developed in collaboration with GÉOCLEAN Ltd. and ADEME agency in France in order to propose a human health risk-based assessment tool.

DISCUSSION

The risk assessment must lead to the final decision making (no action, remediation,...) and if necessary to the fixation of the remedial objectives, based on the human health effects caused by the exposure to a hazardous waste site. This step consists in calculating for an human receptor and for a specific land use scenario the exposure rate through multiple pathways to the site pollutants. The calculated exposure is then compared to a reference dose to characterise the acceptability of the risk.

$$E_{i,k} = \frac{C_i * I_i * EF * ED}{EP * BW} \quad (1) \qquad E_{j,k} = \sum_i E_{i,k} \quad (2)$$

then $$R = \sum_k \left(\sum_j \left(\frac{E_{j,k}}{RfD_{j,k}} \right)_j \right)_k = \sum_k R_k \quad (3)$$

With $E_{i,k}$: Exposure rate for the i pathway and the k pollutant ($mg.kg^{-1}.d^{-1}$),
$E_{j,k}$: Exposure rate for the j exposure mode for the k pollutant ($mg.kg^{-1}.d^{-1}$),
$RfD_{j,k}$: Reference dose for the j exposure mode ($mg.kg^{-1}.d^{-1}$),
C_i : Concentration in the i contact medium ($mg.l^{-1}$ or $mg.m^{-3}$ or $mg.kg^{-1}$),
I_i : Intake rate for the i pathway ($l.d^{-1}$ or $m^3.d^{-1}$ or $kg.d^{-1}$),
R_k : Risk due to the k pollutant,
EF : Exposure frequency ($d.year^{-1}$),
ED : Exposure duration (year),
EP : Exposure period (d),
BW : Body weight (kg).

The TRACES risk assessment module integrates 10 exposure pathways, 3 exposure modes and 8 scenarios of land use as described in table 1.

Exposure scenarios	Exposure modes	Exposure pathways
- Residential on-site	- Inhalation	- Inhalation of air
- Residential off-site		- Inhalation of dust
- Commercial, industrial on-site	- Ingestion	- Ingestion of soil
- Commercial, industrial off-site		- Ingestion of water
- Agricultural, on-site		- Ingestion of meat
- Agricultural, off-site		- Ingestion of fish
- No use, on-site		- Ingestion of fruits and vegetables
- No use, off-site		- Ingestion of dairy products
	- Dermal contact	- Dermal contact with soil
		- Dermal contact with water

Table 1 : Exposure scenarios and exposure routes integrated in TRACES

In order to take into account the uncertainty and the variability of the assessment, many improvements were added to the baseline risk assessment :

- sensibility analysis : by varying manually the values. It is the case of the concentrations measured (mean, maximum and minimum values) and of the accepted cancer risk (10^{-4}, 10^{-5} or 10^{-6}),

- uncertainty analysis : by entering a statistical distribution of a parameter, we can obtain a statistical distribution of the exposure and then of the risk. It is the case of the exposure factors (see table 2).

Exposure factors	Child mean (standard deviation) values	Adult mean (standard deviation) values	Units
Body weight	27 (14)	66 (14)	kg
Skin area	0.95 (0.35)	1.7 (0.2)	m^2
Air inhalation rate	0.03 (0.0044)	0.018 (0.0052)	$m^3.kg^{-1}.h^{-1}$
Water ingestion rate	0.05 (0.02)	0.03 (0.01)	$l.kg^{-1}.d^{-1}$
Soil ingestion rate	97 (169)	49 (69)	$mg.d^{-1}$
Fruits and vegetables ingestion rate	8,000 (5,000)	4,500 (3,000)	$mg.kg^{-1}.d^{-1}$
Dairy products ingestion rate	14,000 (6,000)	3,300 (1,000)	$mg.kg^{-1}.d^{-1}$
Meat ingestion rate	4,400 (1,000)	2,800 (1,000)	$mg.kg^{-1}.d^{-1}$
Fish ingestion rate	370 (100)	300 (100)	$mg.kg^{-1}.d^{-1}$

Table 2 : Exposure factors mean (and standard deviation) values used in TRACES

Based on these improvements, clean-up objectives can be determined, knowing the distribution of the exposure (and then the risk) and the confidence limit of the risk assessment.

REFERENCES

Gephart, L.A., Tell J.G. and Triemer L.R. (1994) Exposure factors manual, *J. of Soil Contamination*, 3(1), 71 pages.

United States Environmental Protection Agency (1989) *Risk assessment guidance for Superfund, vol. 1, Human health evaluation manual*, EPA/540/1-89/002.

Covello V.T. and Merkhofer M.W. (1993) Risk assessment methods : Approaches for assessing health and environmental risks, Plenum Press, New-York

In Situ Remediation of Trace Metals Polluted Soils : A fast Physical-Chemical Approach for the Choice of Amendments

I. Yousfi [1] and A. Bermond [2]

[1] IPSN\DPRE\SERGD\LESTS BP 6 92265 Fontenay aux roses cedex - France- isabelle.yousfi@ipsn.fr

[2] Institut National Agronomique Laboratoire de Chimie analytique, 16 rue Cl. Bernard 75231 PARIS cedex 05 - France - bermond@inapg.inra.fr

Keys Words : In situ remediation, Toxic metals, Contaminated soils .

Abstract : In order to assess the effectiveness of different amendments to rehabilitate toxic metals contaminated soils, a study of six different solid phases has been undertaken. Then, the amounts released from soils and amended soils have been studied in similar physical chemical conditions, especially taken care to compare the soil solution composition, before and after adding solid phases, at the same pH. The results show that several solid phases can be efficient to remediate toxic trace elements contaminated soils. In addition this study has permit to describe a quick tool to select the best amendment in given physical chemical conditions.

Introduction. The natural abundance of trace elements as Pb, Cd, Zn, or Cu tends to increase in soil due to anthropic inputs such as agriculture fertilisation using sewage sludge or storage of contaminated wastes. In soil, this accumulation can lead to a risk for human health because of the possible passage of these toxic elements in the soil solution where they become available for plant uptake or where they can be leached towards groundwater.

In order to limit this risk, several cleanup pathways have been envisaged. From this point of view, in situ remediation adding solid phases able to fix (irreversibly) toxic elements seems to be an interesting issue. Many studies (Gworek 1992a and 1992b, Wong and Wong 1990, Petruzzelli et al. 1987, Pierzynski and Schwab 1993, Sims and Kline 1991, Taylor et al. 1992) have been then carried out to evaluate the effectiveness of different amendments to rehabilitate soils. In most of them (Gworek 1992a and 1992b, Wong and Wong 1990, Petruzzelli et al. 1987), this evaluation depends on the comparison of toxic element concentrations in plants grown on polluted soils amended or not, but does not taken into account possible change in soil physical-chemical features implying modifications of plant uptake and trace element availability.

Our aim was to estimate, quantitatively, the suitability of several solid phases to limit amounts of trace metals in the soil solution. We have investigated the trace metal amounts released in solution from soils and amended soils in controlled conditions -particularly pH-.We aimed to evaluate the real fixation capacity of a given phase and we expected that the measured effect would not include a possible biological effect due to an input of cations brought by amendment and competition for trace elements during root uptake processes or possible variations of trace element solubility due to pH change, able to occur using liming agent for instance.

Material and methods. Two polluted soils were studied ; the first one (Evin) was contaminated by industrial fallout and highly contained Zn and Pb, the second is a sewage sludge treated soil (Couhins) highly contaminated with Zn and Cd. Six different solid phases were used as amendments

: iron or manganese oxides, organic matter, clay and fly ashes (polluted waste of burning). We evaluated the decrease of toxic trace elements in (soil) solution under two kinds of conditions :

- when samples are leached with an ion exchanger ($Ba(ClO_4)_2$, 0.5M), in order to estimate the effectiveness of each phase to immobilise the more labile fraction of toxic trace elements : the exchangeable cations ;
- when soils are submitted to reducing conditions ($NH_2OH.HCl$, 0.1M solution).

The soil sample (1 g), plus solid phase (from 1 to 2% w/w) for « amended soil » study, and the reagent ($Ba(ClO_4)_2$ or $NH_2OH.HCl$, 50 ml) were shaken with mechanical stirrer, for equilibration time. The pH of the solution, pHe, was then measured ; the amounts of trace metals, Zn, Cd, Cu, Pb were measured with a flame atomic absorption spectrophotometer equipped with air-acetylene flame.

Results and discussion. In both media, the effect of added solid phases was estimated from the comparison of the amounts of trace metals released in solution by soil and by the mixing soil+amendment, at the same pH. The amendment effect (E) was calculated as follows :

$$E\,(\%) = 100 * [(R-A) / R]$$

where A is the amount of trace elements released from the mixed soil sample + amendment at a given pHe, A is adjusted of the input of trace elements due to the polluted phase ; R is the amount of trace elements released from the soil sample without amendment at the same pH.

According to the results obtained, several phases seem to be able to improve soil solution quality (clay, MnO_2, contaminated wastes : fly ashes), involving a significant diminution of zinc or/and cadmium concentrations : the greatest decrease (about 90%) is obtained with MnO_2 in exchanger medium. In addition, this study permits to show again that Zn is less labile than Cd, and thus more easy to immobilise.

However, many parameters seem to govern the effectiveness of amendments to rehabilitate polluted soil ; the effects of amendment are then difficult to predict. With this in mind, such a physical chemical approach could be a tool to select the most efficient amendment taking into account physical chemical data.

References.

Gworek B. (1992a.) Inactivation of cadmium in contaminated soils using synthetics zeolite. *Environ. Pollut. 75, 269-271.*

Gworek B. (1992b) Lead inactivation soils by zeolite. *Plant Soil 143, 71-74.*

Petruzzelli G., L. Lubrano, S. Cervelli. (1987) Heavy metals uptake by wheat seedlings grown in fly ash-amended soils. Water Air Soil Pollut. *32(4), 389-397.*

Pierzynski G.M., A.P. Schwab. (1993) Bioavaibility of zinc, cadmium, and lead in a metal- contaminated alluvial soil. *J. Environ. Qual. 22, 247-254.*

Sims J.T., J.S. Kline. (1991) Chemical fractionation and plant uptake of heavy metals in soils amended with co-composted sewage sludge. *J. Environ. Qual. 20, 387-395.*

Taylor R.W., I.O. Ibeabuchi, K.R. Sistani, J.W. Shuford. (1992) Accumulation of heavy metals by legumes and their extractability from acid mine spoil. *J. Environ. Qual. 21, 176-180.*

Wong J.W.C., M.H. Wong. (1990) Effects of ash on yields and elemental composition of two vegetables, *Brassica parachinensis* and *B. chinensis. Agr. Ecosyst. Environ. 30, 251-264.*

PRACTICAL EXPERIENCES OF RISK ASSESSMENT IN ITALY - OPPORTUNITIES ARISING FROM THE FORTHCOMING LEGISLATIVE FRAMEWORK

A. Chiampo and A.O.Thomas

Golder Associates Geoanalysis s.r.l., Via A. Banfo, 43, 10155, Turin, Italy

Keywords: risk assessment, cadmium, zinc, hydrocarbons, USTs

The application of risk assessment to evaluate human health and environmental risks from contaminated sites has generated increased interest from industries, consultancies and the Regulatory Agencies in Italy during the last 5 years.

At present (January 1998) risk assessment is not incorporated in the national legislation, although the new environmental law on remediation of contaminated land (D. Lgs. n. 22/97, - Ronchi Law), drafted in February 1997 and currently under implementation, will very likely contain some risk assessment based methodology. At present, in the absence of national legislation, some Regional Authorities have drafted and implemented more advanced environmental legislation on soil and groundwater remediation, which differ substantially with respect to the acceptance of risk assessment, spanning from a complete acceptance (e.g. Piedmont, Tuscany), to a more limited approach (e.g. Lombardy).

Golder Associates Geoanalysis s.r.l. has since 1995 widely approached environmental problems through the use of risk assessment based methodology; a brief description of two key case histories is hereby provided.

The first case refers to a settling pond, formerly used as waste water treatment plant by a domestic appliances production plant located in the north of Milan, Italy, and discontinued in March 1995. Soil and sludge sediments collected from the pond indicated diffuse contamination due to heavy metals, with cadmium and zinc largely exceeding the Lombardy region soil clean-up standards. The case was extremely delicate because the facility was adjacent to a very sensitive marshy environment, protected by a regional decree.

The initial request of the regulators was a dig-and-dump approach, involving the landfilling of more than 12,000 m^3 of soil with costs largely exceeding 800.000 US$. Following many discussions with the local regulatory and sanitary authorities a risk assessment based remediation strategy was agreed, following the US EPA methodology (USEPA, 1992). The conceptual model indicated that no human health concern exists, as all the potential pathways were non active; however, a very sensitive pathway existed between the leakage from the impacted sediments into the groundwater potentially recharging the surface water, a primary habitat of many sensitive species populating the marsh.

Contaminated Soil '98, Thomas Telford, London, 1998, 1023–1024

Subsequent groundwater solute transport modelling showed that due to local natural conditions (e.g. neutral groundwater pH, slow flow velocity) no substantial contaminant transport occurred at the concentration found in the soil. Further groundwater simulation based on back calculation proved that both zinc and cadmium could not affect the surface water even at solubility limits in the groundwater. Based on these results a closure plan was prepared based on capping with limestone.

The local regulators were intensively involved during the study, and all sensitive assumptions and parameters used in the simulations were discussed with them before being utilised; the closure plan was accepted in December 1996 and the area has been reclaimed and integrated into the marshy protected area. Site works were completed in late spring 1997 and final cost have been reduced to less than 150.000 US$.

A second application of risk assessment has been undertaken at a series of retailing petrol stations of a major oil company impacted by release of hydrocarbons from underground storage tanks (USTs); in this case the study was carried out according to the ASTM Risk Based Corrective Action (RBCA) methodology (ASTM, 1995).

Ten heavily impacted petrol stations were screened out on the basis of the environmental site investigation carried out by Golder Associates on more than 100 service stations. The selected stations were located throughout Italy, spanning sizewise from small kiosk to large motorway filling stations and with widely different local conditions (e.g. geology and hydrogeology).

Initially a Tier 1 screening was conducted; the ASTM "look-up" tables were tailored to the average Italian conditions, though no significant changes were needed. The results showed that the accumulations of hydrocarbon vapours in enclosed spaces was the most significant pathway, followed by impact to the groundwater.

A Tier 2 study was carried out at a retailing station which exceeded the ASTM "look-up" table, and site-specific risk-based remediation criteria were obtained. These remediation targets were found to largely differ from the existing regional soil and groundwater clean-up criteria, these latter being between 50 times (for groundwater) and 100 times (for soil) more stringent than site-specific criteria.

A remediation project has been implemented at the service station in February 1997 and discussion have been currently started with the local regulatory authorities to propose these risk-based remediation criteria as the remediation targets.

ASTM (1995) *Standard Guide for Risk-Based Corrective Action at Petroleum Release Sites E 1739 - 95*, American Society of Standards and Materials, PA, USA

US Environmental Protection Agency (1992) *Risk Assessment Guidance for Superfund, Vol 1, Human Health Evaluation Manual, Part A*, US EPA/540/1-89/002

HEAVY METAL CONTAMINATION AND SOIL MICROARTHROPODS

R.O. Butovsky[1] and N.M. van Straalen[2]

[1] All-Russian Research Institute for Nature Protection, Sadki-Znamenskoje, Moscow, Russian Federation
[2] Vrije Universiteit, 1087, De Boelelaan 1081 HV, Amsterdam, The Netherlands

Key words: biomonitoring, cadmium, contaminated soil, copper, zinc

SUMMARY
Samples of soil microarthropods (Collembola, Mesostigmata, Oribatida) were taken in the Moscow region from 7 sites located in pine forests with different history of heavy metal contamination. The abundance of Mesostigmata and oribatid mites decreased on most heavily polluted sites, whereas it was stable in case of collembolans. Changes of species composition as related to the pollution level have been observed for both groups of mites. Copper and zinc concentrations have been measured in 26 species of oribatid mites. The use of a few indicator species was supposed to be appropriate for decision-making.

The main aim of the project was to study heavy metal impact on soil microarthropods in pine forests of Moscow and Moscow region. Samples were taken from 2 sites located at different distances from a highway, 2 sites located close to chemical plant (Woskresensk), 2 recreation areas in Moscow (Serbryany bor and Losiny Ostrov) and Prioksko-Terrasny State Biosphere Reserve, which was considered as a referent site. Heavy metal concentrations (Cu, Zn, Pb and Fe), organic matter, pH, water content, water soluble and exchangeable fractions of heavy metals were determined in soil samples. The heavy metal concentrations were the lowest at a control site and the highest along the highway and nearby chemical plant. The polluted areas had elevated pH levels, and the lowest water soluble and exchangeable fractions especially for the essential metals.

The relative abundance of Mesostigmata, Oribatida and Collembola and the species composition of the former two groups have been investigated. For oribatid mites the highest abundance was found in the clean sites (up to 38.000 individuals per square meter) whereas in polluted sites it was low (3.000-10.000). The abundance of collembolans has not correlated with the level of pollution, and the abundance of Mesostigmata mites has intermediate sensitivity between these two groups.

Oribatid mites are known as animals with intermediate-high concentration of cadmium in bodies, intermediate-low cadmium assimilation, and low excretion rate (Janssen, 1991). These animals belong to organisms with high cadmium concentration (van Straalen, van Wensem, 1986) as well as to the group of species which are supposed to be heavy metal's deconcentrators (Dallinger, 1993). Heavy metal

concentrations were measured in 26 species of oribatid mites and seemed to be species-specific. Oribatid mites have accumulated from 5.9 to 84.0 ppm of Cu, and from 117.9 to 1069.8 ppm of Zn. High metal concentrations have been found at the Woskresensk area and along the highway (the most polluted sites), while in the Prioksko-Terrasny State Reserve the concentrations were low. The reliable predictions could only be made for *Plalynothrus peltifer, Phthiracaridae* and *Euzetus globulus* (Table).

Table

Mean values of different metals with standard deviations for *Platynothrus peltifer* from different sites. Means are marked with an 'a' if they differ significantly ($p<0.05$) from the reference value (Prioksko-Terrasny State Reserve). When there was no significant difference the data were marked with 'b'. When the data were marked with 'c'. no homogeneity of variances was found. The numbers between the bars give the number of samples measured. Data of Janssen & Hogervorst (1993) at Spanderswoud (The Netherlands) are given for comparison.

Sites*	Heavy metals		
	Zn	Cu	Cd
1	293.6 ±124.4(3)	32.1 ±9.9 (3)	1.5 ± 0.1 (2)
2	570.9(a)±125.8(10)	30.2(c)± 8.9(10)	1.7(b)± 0.6(10)
3	521.6(a)±101.7(6)	24.9(b)± 8.0(6)	1.0(a)± 0.3(7)
4	571.9(a)±124.8(8)	22.2(b)± 6.7(8)	2.2(a)± 0.4(8)
5	589.8(a)±171.8(10)	16.9(a)± 5.5(10)	2.0(b)± 0.4(8)
6	467.8(a)± 64.5(10)	14.1(a)± 4.0(10)	1.3(b)± 0.4(10)
7	311.3(b)± 78.8(10)	17.8(a)± 6.3(10)	2.4(a)± 0.2(10)
8	266.0	21.7	1.4

* Sampling sites: 1 - Prioksko-Terrasny State Reserve. 2 - Losiny Ostrov. 3 - Serebryany Bor. 4 - Woskresensk I. 5 - Woskresensk II. 6 - 10 meters from the highway. 7 - 100 m from the highway. 8 - Spanderswoud.

All described results have been obtained due to NATO Collaborative Research Grant No. 931189.

REFERENCES

Dallinger, R. (1993) Strategies of metal detoxification in terrestrial invertebrates, in Dallinger, R. and Rainbow, P.S. (eds.) Ecotoxicology of Metals in Invertebrates Lewis Publishers, Boca Raton, Florida, pp. 245-289.

Janssen, M.P.M. (1991) *Turnover of cadmium through soil arthropods*, Vrije Universiteit, Amsterdam.

Janssen, M.P.M. and Hogervorst, R.F. (1993) Metal accumulation in soil arthropods in relation to micro-nutrients, *Environmental Pollution 79, 181-189.*

van Straalen N.M. and van Wensem, J. (1986) Heavy metal content of forest litter arthropods as related to to body-size and trophic level, *Environmental Pollution 42, 209-221.*

A Brief Review of the Use of Risk Assessment Software for the Characterisation of Contaminated Land

J. S. Plunkett, D. P. Giles, and N. J. Langdon
Contaminated Land Research Group, University of Portsmouth, Burnaby Building, Burnaby Road, Portsmouth, Hants. PO1 3QL

Summary
This paper summarises the results of a study into the use of computer software for the assessment of human health risks associated with contaminated land. Data from a contaminated site in Portsmouth, Hampshire was used both to benchmark and validate the tested software.

Keywords: Computer Model, Contaminated Sites, Human Health Risk, Risk Assessment.

Introduction
Assessing the risks associated with contaminated land is a major aspect of any brownfield site investigation, as the level of risk posed by any contaminants present will inevitably influence the amount of remedial action necessary. However, the assessment of such risks is a complex and often time consuming process . Advances in the computational capabilities of modern computer systems has facilitated the development of computer based risk assessment software. This paper provides a brief overview of a study evaluating the usefulness and applicability of such software, using data from a contaminated site in Portsmouth, Hampshire.

Risk Assessment Software
Several computer based risk assessment software packages are currently available for use in the assessment of the human health risks associated with contaminated land. The aim of these packages is to calculate estimates of risk using site specific data and a reference database of environmental quality standards. Some of the packages currently available include *Risk*Assistant, EMAGIS, Risc*, and *Risc Human*. The majority of these packages utilise the American Environmental Protection Agency (U.S.EPA) Risk Assessment Guidelines (U.S.EPA, 1987), with *Risc Human* the only package to use the Dutch 'A-B-C' standards (Moen, 1986). In order to evaluate the usefulness and applicability of these packages for use in the United Kingdom (UK) a trial was designed using *Risk*Assistant* and *EMAGIS* with data from the Portsmouth site.

Study Site
The site covers an area of 3.2 hectares and was, like many areas in Portsmouth, reclaimed from the sea using a variety of fill materials over the past 100 years. Over this period the site has been the location of a domestic waste destructor, a highways depot, public allotments and a war time military dump. Chemical analyses of samples taken during previous site investigations have shown that the contamination across this site is varied, with significant levels of Polycyclic Aromatic Hydrocarbons (PAH's), Arsenic, Lead and Mercury predominating.

Practical Application of Software
The software requirements and features of the packages used in this study, *Risk*Assistant* and *EMAGIS,* are summarised in Table 1. *EMAGIS* adopts a spatial approach to the risk assessment whereas *Risk*Assistant* utilises a more site/sample model.

Package	Requirements	Features
*Risk*Assistant*	Windows	User defined exposure scenarios, interactive sensitivity analysis, multisample spreadsheet and aggregation facility, 4 Hazard data sources(IRIS, HEAST, HazData NJ, HazData CA), Air Dispersion Model (Win-ISC2), Stream*Model.
EMAGIS	Windows, MapInfo, Excel, Surfer	User defined exposure scenarios, contouring module, cross section generator, contaminant correlations module, statistical trend analysis, soil concentration profile generator, 2 toxicity databases (USEPA, Cal/EPA).

Table 1: Software Requirements and Features of Tested Software in Initial Trial

To calculate risk estimates both of these systems follow the *Source-Pathway-Target* methodology as illustrated in Figure 1.

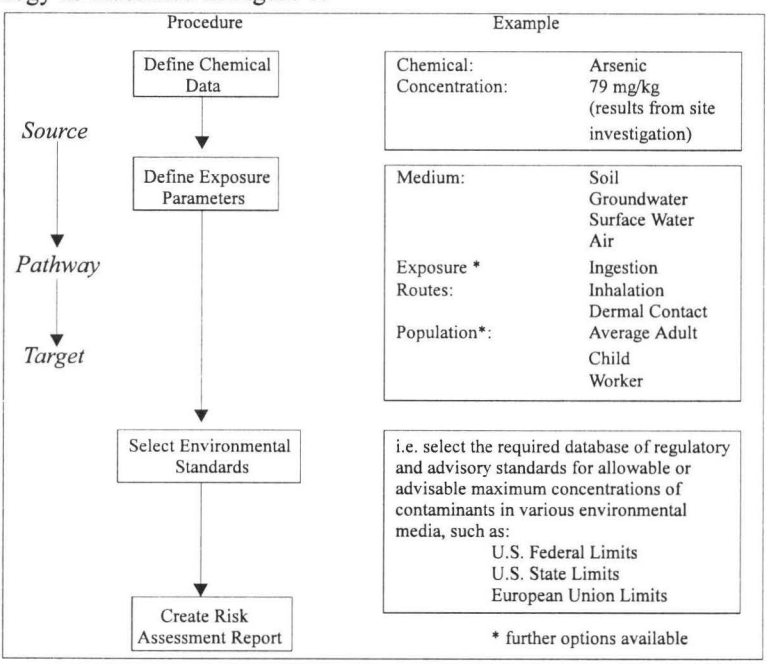


Figure 1: Procedure for estimating human health risks using risk assessment software.

Conclusions

The initial results of this study have shown that although the software packages are quick and simple to use, the results produced depend greatly on the amount of data input into the system and on the user, i.e the level of knowledge the user has of the risk assessment process and the users competence with computers. As both of the systems used in this trial utilise U.S. guidelines, the results produced can only be used in the UK for guidance purposes but even on this basis these systems can be useful tools in the characterisation of contaminated sites.

References

U.S.EPA. (1987) *The Risk Assessment Guidelines of 1986.* Office of Health and Environmental Assessment, Washington, DC. EPA/600/S9-85/001F.

Moen, J.E.T. et al (1986) Soil protection and remedial actions: Criteria for decision making and standardisation of requirements. In: Assink, J.W. and Van den Brink, W.J. (eds) *Contaminated Soils.* Martinus Nijfaff. Dordrecht. pp. 441-448

Towards Quantitative Risk Assessment - A Case History

A S O'Brien
Mott MacDonald, Croydon, UK

Key Words
Risk assessment, case study, Benzene, Naphthalene, natural attenuation.

Introduction

This paper describes the application of relatively simple quantitative models to assess the migration of dissolved phase contaminants in groundwater, and associated human health risk. The model predictions are compared with the results of monitoring both inside and beyond the boundary of a contaminated site. The soil profile comprised made ground (about 2.5 to 3.5m thick) overlying glacial clay. The made ground was predominantly granular, with some discontinuous clayey layers and a permeability of about 5×10^{-5}m/s. Benzene and Naphthalene were identified in elevated concentrations in groundwater. The site was located in a light industrial area with a "hard" site cover.

Quantitative Risk Assessment

The contaminant source was encapsulated, however there was evidence which suggested that off site migration of contaminated groundwater had already occurred. Contaminant transport modelling and human health risk assessments were carried out to assess if the long term risks associated with the residual off site contaminant plume were significant or not. The risk assessment techniques used were Risc-human (described by Goldsborough and Smit 1995 and Goldsborough 1988), and CVM (described by OGI, 1995).

Figures 1 and 2 show measured time dependent changes following source isolation for Benzene and Naphthalene concentrations respectively, and these are compared with predicted changes. The predicted reductions with time are slower than measured values. However, the marked difference in time dependent behaviour between Benzene and Naphthalene is correctly predicted. CVM simulations were carried out to achieve a best fit with the monitoring data. These indicated a half life for Benzene of about 0.2 to 0.25 years, compared with the original predictions, based on a half life of 0.5 years. This compares with half lives for Benzene quoted in the literature varying between 0.4 and 1.0 year (Hubbard, 1994, King, 1995 and Verschueren, 1996). For Naphthalene the back analysis was more uncertain, nevertheless a half life of between 1 and 5 years was estimated. Data in the literature gives a range of half life for Naphthalene varying between 1.3 and 8.2 years. Table 1 summarises the results of the Risc-human analyses which highlight the influence of organic matter content, depth and type of contaminant. Given the type of site use and relevant exposure pathways the risks associated with Benzene were significantly higher than those for Naphthalene. Primarily due to Benzene being relatively volatile. From these analyses it was judged that the risk to adjacent land users in the future would reduce to relatively low levels, once Benzene concentrations had reduced. The monitoring and modelling showed that Benzene concentrations would reduce to relatively low concentrations quite quickly after slurry wall installation.

Conclusions

The use of the numerical models described herein proved to be valuable tools in allowing rational judgements to be made about site-specific risks (both current and future). These types of models are particularly helpful in comparing the relative risks associated with different contaminants, and the relative merits of different remediation strategies to be

Contaminated Soil '98, Thomas Telford, London, 1998, 1029–1030

assessed. However, extreme caution should be exercised when predicting absolute values at a given point in time or distance due to the uncertainty which can be associated with many input variables. Calibration of models by site specific monitoring is very important.

References

Goldsborough and Smith, 1994. Modelling of human exposure to soil pollution, computer models for risk assessment. June 1995.

Hubbard et al 1994. Transport and fate of dissolved methanol, MTBE and monoaromatic hydrocarbons in a shallow sand aquifer. American Petroleum Institute Publication 4601.API, 1200L st. NW, Washington DC 2005, USA

King et al 1995. Natural attenuation of coal tar organics in groundwater. Proceedings 3rd International Symposium : in situ and on site bioreclamation, Battelle, San Diego, 1995.

Oxford Geotechnica Ltd 1995. CVM, a finite element model for the analysis of transient groundwater flow and contaminant transport.

Verschueren, 1996. Handbook of Environmental Data on Organic Chemicals, 3rd Edition. Published by Van Nostrand Reinhold.

Contaminant	Concentration (mg/kg)	Depth (m)	Organic Matter Content (%)	Lifetime Average Daily Dose (LADD) (mg/kg/day)	Risk Factor (LADD) (MTR)
Benzene	2	1.25	10	7.4×10^{-3}	1.7
Benzene	2	1.25	2	0.031	7.2
Benzene	2	2.5	10	1.46×10^{-3}	0.34
Naphthalene	170	1.25	10	1.5×10^{-3}	0.03
Naphthalene	170	1.25	2	7.6×10^{-3}	0.15

Note: MTR = Maximal Tolerable Risk Level
Benzene, vapour pressure = 76 mm Hg
Naphthalene, vapour pressure = 1.0 mm Hg
Exposure routes – vapour inhalation, permeation of drinking water pipes

Table 1 - Results of Selected Risc Human Sensitivity Analyses

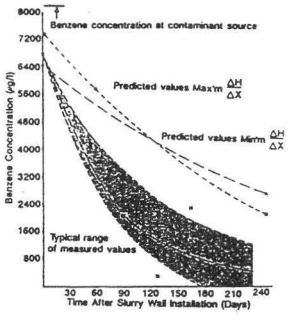


Figure 1 : Decay Rate for Benzene 4 m from Source

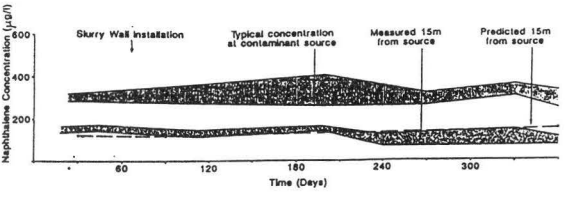


Figure 2 : Decay Rate for Naphthalene 15 m from Source

RELEASE KINETICS OF 4-CYANOPHENOL FROM SOIL INTO CELLULOSIC MEMBRANES

Scott M. Arnold[1], Annette L. Bunge[2] and Richard H. Guy[3]
[1] Ecology and Environment, Inc., 840 K Street, Ste 100, Anchorage, AK 99501 USA
[2] Dept. Chemical Engr. & Petroleum Refining, Colorado School of Mines, Golden, Colorado 80401 USA
[3] Centre Interuniversitaire de Recherche et d'Enseignement, Campus Universitaire, Parc d'Affaires International, F-74166 Archamps, France

Keywords: contaminated soil, dermal absorption, human health risk, risk assessment, exposure

INTRODUCTION

Surface soils contaminated with toxic chemicals are found at many industrial, agricultural and residential sites. Health risks from dermal exposure to such soils depend on the amount of chemical absorbed and its toxicological potency. If skin were a perfect barrier, then exposure to even highly toxic chemicals would cause no adverse health effects. However, skin is a permeable membrane, particularly to lipophilic chemicals of modest size (< about 500 Da), and the potential exists, therefore, for adverse health effects following dermal exposure to contaminated soils. Unfortunately, methods used to estimate dermal absorption from contaminated soils are based on poorly quantified parameters. Experimental studies are limited (only a few chemicals have been measured from even fewer soils), and the data available may significantly under-represent dermal absorption[2].

The goal of our research on contaminated soils is to develop and to experimentally validate predictive procedures to estimate dermal absorption from the level of chemical contamination and the basic properties of the soil (e.g., particle size distributions, moisture content and organic carbon content). In the course of this work, we have measured the uptake of 4-cyanophenol (4CP) from soil into (a) human stratum corneum *in vivo*[3], (b) hairless mouse skin *in vitro*[3], and (c) polymeric membranes of mixed (acetate/nitrate) cellulose esters (CM). The CM experiments are described here.

EXPERIMENTAL METHODS

The rate of 4-cyanophenol [cyano-^{14}C] transfer to CM was measured as a function of time (up to 100 hrs) from fresh and aged (~ 5 months) soils contaminated at three different levels of chemical (0.001, 3 and 30 mg of 4CP/g soil). The <250 μm fraction of two soils (a clay loam (CSU) and a silty clay loam (ISU) with organic carbon content of about 1 and 3 wt %, respectively) were studied. The porous CM (Type HATF from Millipore, Bedford, MA) from a single lot (No. H6CM0645) were 150 μm thick, with 0.45 μm nominal pore diameter. Treatment area was ~ 0.7 cm^2. 4CP dissolved in 1.5 mL of acetone was added to 5 g of soil, which was air dried for 24 hours and then placed on a wrist-action shaker for an additional 24 hours. The CM sat on a nonabsorbing surface (aluminum foil) and sufficient soil was placed on top of each CM to completely coat the treatment area (~200 mg/cm^2). The entire experiment was enclosed to prevent evaporation, which was confirmed by analysis of each soil sample at the conclusion of each experiment. At the beginning of an experiment, the contaminated soil was divided among enough CM samples to produce replicate measurements (n = 2 or 3) for all time points. Periodially, soil was removed from the CM, and the CM was dissolved in 10 mL of scintillation cocktail (Packard Econofluor-2) and then analyzed by liquid scintillation counting. A few results are presented for *in vivo* human skin and *in vitro* hairless mouse skin experiments. In these experiments, the treatment area of the skin was completely covered by soil that was prepared and contaminated as for the CM experiments.

RESULTS AND DISCUSSION

Figs. 1 and 2 show the mass of 4CP uptake into the CM normalized by the contamination level on the soil (i.e., M_{uptake}/C_{soil}), plotted as a function of time. Each symbol denotes the mean value of replicate measurements (n = 2 or 3) for a separately contaminated soil sample; error bars, representing ± 1 standard deviation, are indicated but not always visible. When the mass of soil on the skin is constant (as it was in these experiments), then M_{uptake}/C_{soil} is proportional to the % released from the soil (= % absorbed by the membrane). The results from freshly contaminated CSU and ISU soils are

shown in Fig. 1. CM uptake from aged soil are compared to freshly contaminated soil for CSU in Fig. 2.

As shown in Figs. 1 and 2, normalized 4CP uptake from the freshly contaminated soils appears to be insensitive to the difference in organic carbon content between the CSU and ISU. For contamination levels of 0.001 and 3 mg/g, the normalized uptake during the first 24 hours was essentially constant at 12 $\mu g/cm^2/hr$, indicating that uptake is proportional to concentration at these levels of contamination. However, normalized uptake increased substantially to 120 $\mu g/cm^2/hr$, when the contamination level was increased to 30 mg/g for both soils. That is, increasing the soil contamination from 3 to 30 mg/g resulted in a *100-fold* increase in uptake. This effect was also observed in experiments of hairless mouse skin *in vitro* with the CSU soil (normalized flux was 11 $\mu g/cm^2/hr$ for 4CP concentrations of 0.18 and 5 mg/g soil and 120 $\mu g/cm^2/hr$ for concentrations of 50 mg/g). Normalized flux results for CM and hairless mouse skin (*in vitro*) are comparable to that observed for human skin *in vivo* (68 $\mu g/cm^2/hr$ for 50 mg of 4CP/g soil). Soil aging had almost no effect on the normalized uptake for the ISU soil (data not shown). However, uptake from aged CSU, contaminated at 0.001 mg/g, was about 2-3 fold higher than from freshly contaminated CSU (Fig. 2). It should also be noted that uptake from the CSU soil was affected strongly by temperature, suggesting that contaminant vapor pressure may affect kinetics (data not shown).

CONCLUSIONS

Many methods for estimating dermal absorption from soil-borne contaminants utilize absorption efficiencies, and some regulatory agencies have proposed default values for large chemical classes (e.g., the California EPA recommends assuming that 15% of any polynuclear aromatic hydrocarbon would dermally absorb from soil). This approach is inconsistent with the results of this study, which show that absorption efficiency (i.e., the normalized uptake) is not constant, even for a single chemical. Specifically, normalized uptake of 4CP into cellulosic membranes and hairless mouse skin varied with chemical concentration on the soil and the time the soil was in contact with skin.

REFERENCES CITED

1. J.E. Johnson and J.C. Kissel, *Human & Ecolog. Risk Assess.* **2**, 356-365 (1996).
2. A.L. Bunge and J.M. Parks, Environmental Toxicology and Risk Assessment: Modeling and Risk Assessment ASTM STP 1317, Eds. F.J. Dwyer, T.R. Doane, M.L. Hinman, ASTM, W. Conshohocken, PA, 227-244 (1997).
3. G.D. Touraille, A.L. Stinchcomb, F. Pirot, R.H. Guy, A.L. Bunge, J.P. Marty, Proc. of Controlled Release Society Mtg., Stockholm, Sweden, June 15-19 (1997).

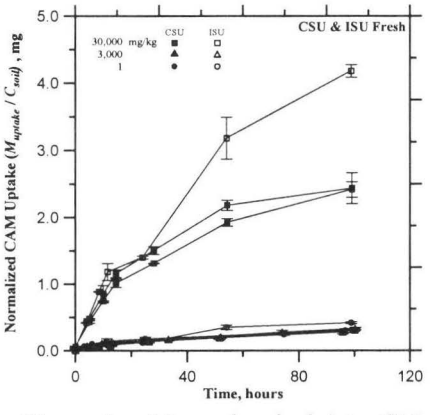


Figure 1. Mass absorbed into CM (uptake) from freshly contaminated CSU and ISU soil normalized by 4CP soil concentration.

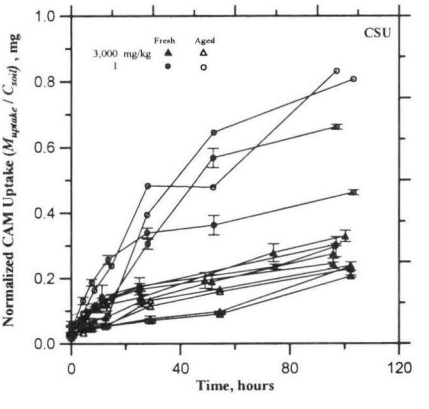


Figure 2. Mass absorbed into CM (uptake) from fresh and aged contaminated CSU soil normalized by 4CP soil concentration.

Soil quality standards: a comparative study

Demetrio Pitea, Elena Collina, Marina Lasagni, Raffaella Ligorati

Dipartimento di Chimica Fisica ed Elettrochimica, Università degli Studi di Milano via C. Golgi, 19 - 20133 Milano - Italy

Keywords: contaminated sites, quality standards

Soil quality standards are used to decide whether a contaminated site should be remediated or not. Guidelines to assess contaminated soil quality vary throughout the world. Generally, standard and trigger values are defined taking into account local background levels and in order to protect human health and the environment.
In Italy is presently still missing a specific national legislation concerning soil quality assessment and contaminated sites remediation. Some Italian regions (Piemonte, Tuscany, Lombardia) developed a number of different guidelines based on protocols in use abroad, *e.g.* the Dutch *AC* guidelines and the Canadian guidelines.

In the framework of a project funded by the Italian National Research Council for the development of a general strategy for the management and remediation of contaminated soils, three different soil quality standards (Dutch, Canadian and Piemonte Region) were applied and the results obtained compared. The aim was to verify if a univocal classification is achieved.
The test was carried out on a former industrial site near Lodi, Italy, which presented diffuse contamination. In the past years, a large number of chemical analyses were performed on soil and groundwater samples collected on the site (Table 1). Thus, the situation is further complicated by the different laboratory practices and methods used for analysing contaminants which led, in some cases, to very different results.

Table 1 - Data collected in different sampling campaigns.

Sampling period	Laboratory	Samples	Analytical parameters		Data
			Inorganic	Organic	
1993	Lab1	11 - soil	7	12	209
1993	Lab2	23 - soil	13	6	437
1995	Lab3	12 - soil	10	5	180
May 1996	Lab4	19 - soil	11	44	1045
May 1996	Lab4	9 - water	19	44	567
October 1996	Lab4	23 - water	19	182	4623

First, the three guidelines chosen were applied to every single data set. In any case, the final classification stated the need for site remediation.
To obtain a clearer result, we derived a unique data set calculating for every data set the mean value for every parameter, and finally by determining the mean value of the means. Application of the three guidelines to these data led almost to the same results (Table 2).

Table 2 - Compounds for which clean-up is needed (☹) or not (☺) according to three different guidelines.

Compound	*Dutch*	*Canadian*	*Piemonte*
pH	-	-	☹
As	☹	☹	☹
Cu	☹	☺	☹
Hg	☹	☹	☹
Dichloromethane	☹	☹	☹
Tetrachloroethene	☹	☺	☹
Benzene	☹	☹	☺
Naphtalene	☹	☹	☹
Anthracene	☹	-	☹
Phenanthrene	☹	☹	☹
Fluoranthene	☹	-	☹
Benzoanthracene	☹	☹	☹
Pyrene	-	☹	☹
PAH	☹	-	☺
Phenols	-	-	☹

We could notice that the data were non-homogeneous, and the final mean values were heavily influenced by some dispersed values. Therefore, as a new methodology, we propose to calculate the final mean value by weighing the mean of each data set by the standard deviation. So, the influence of most widespread data is reduced. In fact, the classification with respect to one parameter, *i.e.* arsenic, changed, as just one soil sample presented a very high concentration of this metal.

QUANTIFYING THE RISK POSED TO GROUNDWATER FROM COMTAMINATED LAND - THE CONSIM MODEL

D.H. Hall[1], R.C. Harris[2], S. Moncaster[1], B. Plimmer[1] and M. Rogers[1]

[1]Golder Associates (UK) Ltd., Edwalton, Nottingham, NG12 4DG, UK.
[2]Environment Agency, Olton Court, Solihull, West Midlands, UK

Key words: Risk assessment, computer simulation, contaminated sites, groundwater, biodegradation, remediation.

SUMMARY: The ConSim model is a tool for the assessment of groundwater pollution potential resulting from the contamination of soils that will find widespread application with regulators, developers and their advisors. The model allows the source and pathways to be defined in such a way that uncertainty is fully addressed. The model includes a module that will generate leachate data from soil chemical data, allows retardation and biodegradation within all pathways, and includes an analytical model of 2-D advective, dispersive flow to a receptor.

INTRODUCTION

ConSim has been developed by Golder Associates on behalf of the Environment Agency to provide regulators (and those concerned with contaminated land) with software capable of quantitatively assessing the risk posed to groundwater by contaminated land. The program uses site investigation data and specific chemical properties to model contaminant mobilisation, transport though the vadose zone, dilution within an aquifer, and concentrations of contaminants at a receptor. Retardation of chemical species and first order biodegradation (or radioactive decay) processes can be modelled.

THE ConSim MODEL

The model allows the assessment of contaminated land (within the context of its impact on groundwater), by following a structured and formalised approach that both adjusts to the degree of information available and deals with inherent uncertainty. Although the model allows only relatively simple problems to be assessed, one of the secondary objectives of the model's development is to highlight the data that should be collected from a typical site investigation so that the impacts on groundwater quality can be addressed.

ConSim performs risk estimation by calculating the probability of contaminant concentrations exceeding a specified Water Quality Standard(WQS) or target value. Risk evaluation is implicit in the selection of standards that are appropriate for the situation being assessed.

The initial assessment (Tier 1) deals with the comparison of leach test data with a predetermined WQS. In the absence of leach test data, the model will simulate a leachate quality based on soil concentrations, Kds, soil organic carbon content and maximum solubility for the contaminant(s) of interest. If the results of this Tier 1 assessment indicate the WQS has not been exceeded then the analysis is complete and

no remediation is required (for the purposes of groundwater protection). If the Tier 1 assessment fails then either appropriate site investigation data are needed for running a Tier 2 assessment or remediation is deemed necessary.

For a Tier 2 assessment details of the unsaturated zone and dilution potential are required. Within this part of the model processes such as retardation, biodegradation and dilution in groundwater immediately beneath the site are considered Analyses can, again, be terminated at this point if the WQS is not exceeded.

If the results of a Tier 2 assessment show exceedance of the WQS then analyses can progress to Tier 3 where migration and further attenuation and degradation are modelled within the saturated pathway between the source and receptor. Clearly, information and data requirements become more comprehensive (and expensive to obtain), and details of the pathway (which may well be outside the property boundary) will need to be obtained.

The necessary calculations within the model are performed using analytical solutions to groundwater flow and contaminant transport equations. These are solved using data available from site investigation studies or library data. To account for spatial variability in contaminant concentrations and uncertainties in the field data, the calculations are performed probabilistically using a Monte Carlo simulation. There is the facility within the model to describe all data input values as user specified probability density functions.

DISCUSSION

The UK Environment Agency has previously supported the development of the LandSim model that deals solely with the groundwater impact of landfill sites. The ConSim model has drawn heavily on this earlier development and on many of the lessons learnt. The intended users of the model include regulators, consultants, developers, and those with a professional or academic interest in both contaminated land and groundwater.

The structured nature of the model will assist those undertaking the assessment in determining what data is actually important, which has equal importance to the assessment itself. Equally, there is no widely accepted UK model available to regulators that addresses the inherent uncertainties associated with contaminated land and its impact on groundwater. As with LandSim, the ConSim assessment does not provide a simple yes or no answer, but steers both regulator and developer to undertake a properly structured and defensible assessment that will assist in the decision making process.

ACNOWLEDGEMENTS

The development of the model has been undertaken by Golder Associates under contract to the UK Environment Agency. The views expressed in this paper are those of the authors and should not necessarily be interpreted as those of the Environment Agency.

REFERENCES

Gronow, J. and Harris, R.C. 1996, LandSim: A regulatory tool for the assessment of landfill site design. Waste Management, Feb 1996, p 30-32

ASSESSMENT OF DERMAL EXPOSURE TO SOILS

J. Kissel[1], T. Garlock[2] and J. Shirai[1]

[1]Department of Environmental Health, University of Washington, Seattle, WA 98195-7234, USA
[2]Shannon & Wilson, Inc., 400 N. 34th St., Suite 100, P.O. Box 300303, Seattle, WA 98103, USA

Keywords: Contaminated soil, exposure, exposure pathway, human health risk, risk assessment, soil, soil clean-up criteria

Protocols used in the U.S. to assess human exposure to chemicals in soils at contaminated sites usually include a dermal pathway. Use of default exposure factors found in U.S. Environmental Protection Agency (USEPA) guidance can easily lead to dermal route risk projections that appear to warrant remedial action. However, because those default parameters are typically highly uncertain, risk estimates based on them inspire little confidence. Allocation of clean-up resources on the basis of such estimates is problematical. On the other hand, failure to use the results of a risk assessment opens the process to criticism that it is merely a means for post hoc rationalization of preordained conclusions. Better estimates of soil/dermal pathway risk are therefore needed to fully integrate the risk assessment paradigm into the site remediation decision process. Toward that goal, a series of efforts funded by USEPA and the U.S. Department of Energy (USDOE) have been conducted at the University of Washington to improve the empirical grounding of relevant exposure factors. These efforts include field measurement of dermal soil loadings resulting from a variety of activities, phone surveys of behavioral patterns likely to lead to or prolong soil contact, pilot studies of soil contact using soil amended with a fluorescent marker, and laboratory studies of the effect of soil properties on adherence.

Field measurements were obtained by washing hands, forearms, lower legs, faces, and/or feet, filtering the wash water, and weighing dried residue. Two hundred subjects, aged 1 to 67, participated. Groups include children in daycare, children playing in mud, gardeners, rugby players, water utility crews, earth-moving equipment operators, and others. Figure 1 displays geometric mean and corresponding 95% confidence intervals for hand loadings from various groups. Measured hand loadings fall on both sides of the USEPA default range. Results obtained from other surfaces demonstrate that hand loadings are conservative estimators of skin loadings within, but not across, activities.

Telephone surveys have been used to assess rates of participation in selected non-occupational activities likely to lead to soil contact. Two sample populations, each of 450 households, were surveyed. One sample was drawn from the entire U.S., the other from counties surrounding the Hanford nuclear site. Participants were selected using random digit dialing. Questions regarding clothing choices and bathing practices were included to assess skin area exposed and duration of soil contact. Answers were obtained for both warm and cold weather scenarios.

Pilot studies involving staged activities in soil amended with a fluorescent marker were conducted in a greenhouse. Trials included children playing and adults laying pipe. Outcomes were assessed using both video imaging under long-wave UV and gravimetric analysis. Variables examined included clothing, activity duration and soil moisture.

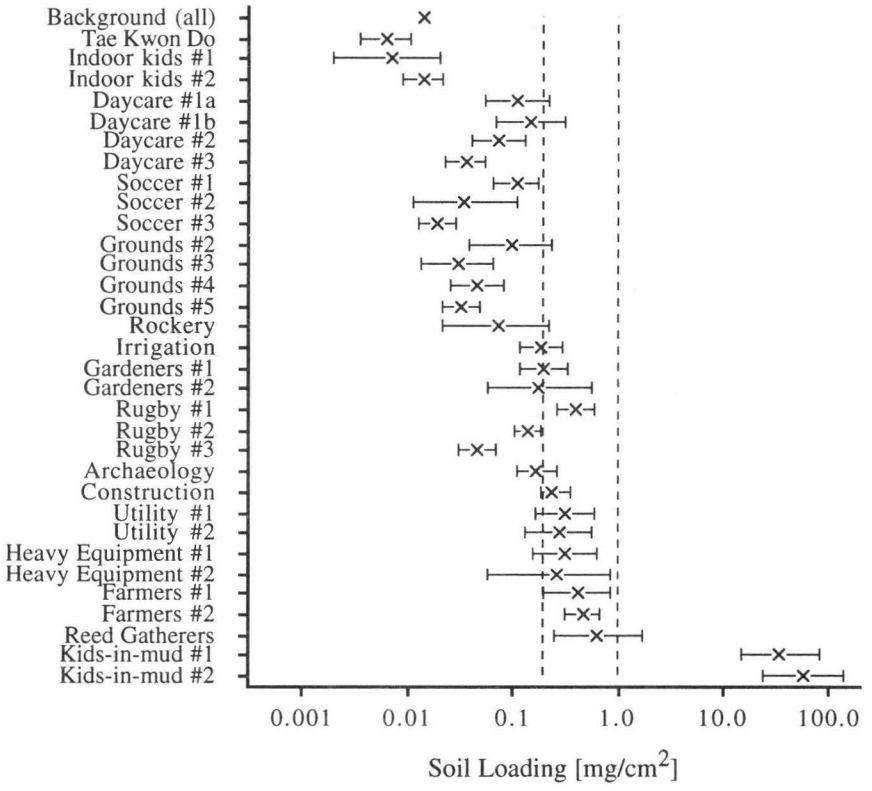


Figure 1. Geometric means and corresponding 95% confidence intervals for hand loadings from field measurements. Vertical dashed lines are bounds of the 1992 USEPA default range.

Volunteers' hands have been artificially loaded in the laboratory by pressing them into soil. Trials have focused on the effects of moisture and particle size on adherence.

Results from all of the studies are currently being integrated to produce a distribution of estimated dermal exposures to soil in residential settings. A residential scenario was selected on the basis of availability of information and pertinence to clean-up decisions.

Funding for this work was provided by the Office of Health and Environmental Assessment, USEPA through Cooperative Agreements R819052-01-0 and CR824065-01-0 and by the USDOE via the Consortium for Risk Evaluation with Stakeholder Participation (DE-FCO1-95EW55084). However, this document has not been reviewed by USEPA or USDOE and should not be assumed to represent agency or department views.

REFERENCES (abbreviated; see http://weber.u.washington.edu/~jkspage/)

Garlock, T. and Kissel, J. "National and Regional Responses to a Survey of Soil Contact Related Behaviors," J. Expos. Anal. Environ. Epid. (in review).

Kissel, J., Richter, K., and Fenske, R. (1996). "Field Measurement of Dermal Soil Loading Attributable to Various Activities: Implications for Exposure Assessment," Risk Anal. 16(1):115-125.

Kissel, J., Richter, K., and Fenske, R. (1996). "Investigation of Factors Affecting Soil Adherence to Skin Using a Hand-Press Technique," Bull. Environ. Contam. Toxicol. 56(5):722-728.

EARTHWORM AVOIDANCE TEST FOR SOIL ASSESSMENT: ALTERNATIVE FOR ACUTE AND REPRODUCTION TEST

K. Hund

Fraunhofer-Institute for Environmental Chemistry and Ecotoxicology
D-57377 Schmallenberg

Key words: bioassays, bioavailability, contaminated soil, ecotoxicological, organic contaminants, risk assessment, soil fauna, toxicity tests

INTRODUCTION

Acute tests using earthworms are proposed for the assessment of contaminated and remediated soils (DECHEMA; 1995). However, contaminants are detected only at comparatively high concentrations. More sensitive than acute tests are sublethal tests, e.g. the reproduction test with earthworms (ISO 11268-2). This test, however, is very time consuming needing long incubation periods with results obtained after 56 days. Therefore, this test is not suitable for a routine assessment of remediated soils. An earthworm avoidance test may be an adequate alternative. In this test, the test vessels contain two kinds of soil, the test soil and an uncontaminated reference soil (control soil). After addition of the worms and an incubation period of two days, the worms in the test soil as well as in the reference soil are counted. It is expected that the worms do not stay in soils which are unfavourable for them. A test design is proposed by Yeardly et al. (1996).

RESULTS

In the presented study the sensitivity of the avoidance test in comparison to the acute and to the repro-test is shown. For the avoidance test soils contaminated with organic substances were used which showed no effect (no mortality) in the acute test, but resulted in a significant reduction of the number of offsprings in the repro-test. As uncontaminated control soil in the repro-test several soils differing in soil structure and C_{org} were used.

Following main results were obtained:

- The sensitivity of the avoidance test seems to be comparable to the sensitivity of the repro-test. However, the test duration is much shorter (2 days vs. 56 days) and the test effort is much lower (no counting of small offsprings).
- The type of the control soil seems to be of subordinate importance. The tendency of the earthworms to leave a soil is mainly influenced by the bioavailable contamination.

Contaminated Soil '98, Thomas Telford, London, 1998, 1039–1040

CONCLUSION

The avoidance test seems to be a good alternative to the repro-test with respect to its sensitivity to indicate the presence of a bioavailable contamination.

REFERENCES

DECHEMA (1995) *Bioassays for soils*, Ad-Hoc Committee "Methods for Toxicological/Ecotoxicological Assessment of Soils", DECHEMA, Frankfurt am Main.

ISO 11268-1 (1993) *Soil quality - Effects of pollutants on earthworms (Eisenia fetida) - Part 1: Determination of acute toxicity using artificial soil substrate.*

ISO/DIS 11268-2 (1993) *Soil quality - Effects of pollutants on earthworms (Eisenia fetida) - Part 2: Method for the determination of effects on reproduction*

Yeardly, R. B., Lazorchak, J.M. and Gast, L.C. (1996) The potential of an earthworm avoidance test for evaluation of hazardous waste sites, *Environ.Toxicol.Chem. 15, 1532-1537.*

TOXICITY TESTING OF POLYCYCLIC AROMATIC HYDROCARBONS WITH THE RHIZOBIUM-LEGUME SYMBIOSIS

H. Neumann, A. Bode-Kirchhoff, A. Wetzel and D. Werner

Department of Biology, Philipps-University of Marburg,
Karl-von-Frisch-Str., 35032 Marburg, Germany
neumann2@mailer.uni-marburg.de

Key words: alfalfa, biotest, ecotoxicity, nodulation, polycyclic aromatic hydrocarbons, *Rhizobium*, symbiosis

SUMMARY
Legume root nodules are the site of biological nitrogen fixation in the legume-*Rhizobium* symbiosis. Nodules are structures unique to this symbiosis and they are morphologically as well as physiologically distinct from other plant organs. Heavy metals affecting the macro- or microsymbionts vitality, such as cadmium and arsenic compounds (Neumann *et al.*, in press), reduce nodulation even before visible damage to the plant can be detected. We present data that the formation of nodules (nodulation) may also serve for ecotoxicological evaluation of polycyclic aromatic hydrocarbons. Tests were performed with alfalfa (lucerne) seedlings inoculated with *Rhizobium meliloti*. A dose responsive decrease in nodulation was found after application of acenaphtene, fluorene, phenanthrene, fluoranthene and benzo(a)pyrene. The dose response curves were used to calculate EC50-values.

ZUSAMMENFASSUNG
Die biologische Stickstoff-Fixierung der Symbiose zwischen Leguminosen und Rhizobien findet in den Wurzelknöllchen der Leguminosen statt. Sie gelten als die spezifischen Organe dieser Symbiose und unterscheiden sich sowohl morphologisch als auch physiologisch von anderen Pflanzenorganen. Schwermetalle wie Cadmium- und Arsenverbindungen beeinflussen die Lebensfähigkeit von Makro- und Mikrosymbiont und hemmen die Knöllchenbildung, bevor eine sichtbare Schädigung der Pflanzen zu beobachten ist (Neumann *et al.*, im Druck). Wir zeigen, daß eine ökotoxikologische Bewertung von polyzyklischen aromatischen Kohlenwasserstoffen anhand der Ausbildung von Wurzelknöllchen möglich ist. Die Tests wurden mit Luzerne-Keimlingen durchgeführt, die zuvor mit *Rhizobium meliloti* beimpft worden waren. Die Prüfsubstanzen Acenaphten, Fluoren, Phenanthren, Fluoranthen und Benzo(a)pyren führten zu einer dosisabhängigen Hemmung der Nodulation. Aus den Dosis-Wirkungsbeziehungen wurden EC50-Werte berechnet.

RÉSUMÉ
La fixation biologique de l'azote de la symbiose *Rhizobium*-légumineuses a lieu dans les nodules radiculaires des légumineuses. Ce sont des structures spécifiques à cette symbiose qui se distinguent morphologiquement et physiologiquement des autres organes végétaux. Des métaux lourds comme les composés de cadmium et d'arsenic affectent la viabilité du macro- et du microsymbiote et inhibitent la nodulation avant même que des lésions visibles de la plante puissent être constatées (Neumann *et al.*, en

press). Nous montrons que la formation de nodules pourrait servir à une évaluation écotoxicologique des hydrocarbures polycycliques aromatiques. Les tests ont été effectués chez des germes de luzerne inoculés avec *Rhizobium meliloti*. Après application des substances acénaphtène, fluorène, phénanthrène et benzo(a)pyrène, une diminution de la nodulation, dépendante de la dose appliquée, fut observée. Les courbes dose-effet furent utilisées pour calculer les valeurs EC50.

There are only a few standardized and widely used assays with higher plants for toxicity testing of PAHs in solid substrates resembling the soil environment. It has already been established that nodulation of legumes by the microsymbiont *Brady-/Rhizobium* is affected by xenobiotics like heavy metals in the field (Angle *et al.*, 1993). Root nodules are the result of two interacting genomes, leading to a continuous metabolic dialogue between higher plants and bacterial cells. They are the site of symbiotic nitrogen fixation. We have developed and standardized a biotest which uses the sensitivity of the nodulation process of *Medicago sativa* by *Rhizobium meliloti* as the effect parameter.

Tests were performed in petri dishes with alfalfa (lucerne) seedlings inoculated with *Rhizobium meliloti*. After mineral medium or standard soil solidified by Gelrite® had been poured into petri dishes, PAHs were sprayed as etheral solutions in different dilutions on the surface of the two media. Furthermore, a mixture of standard soil and sand was prepared and filled into rhizotrons. The sand was supplied with etheral PAH-solution.

Cultivation took place in growth cabinets with carefully standardized and documented growth conditions. Data from stressed plants was recorded after 14 days of cultivation on contaminated substrate such as solidified mineral medium or standard soil.

A dose responsive decrease in nodulation was found after application of the tested PAHs. The relation between different concentrations of the toxicant and the resulting effect on nodulation as biological parameter can be described with an exponential or linear function. Nodulation was reduced even before visible damage to the plant, measured as shoot and root fresh weight can be detected. The toxicity of the tested PAHs in the assay correlated with their water solubility and their n-octanole/water distribution coefficient (K_{OW}) except benzo(a)pyrene. Its toxicity was higher than could be expected by its water solubility and K_{OW}-value.

Tests performed with fluoranthene and phenanthrene contaminated soil in rhizotrons resulted in a weak nodulation inhibiting effect in contrast to tests with mineral medium (fluoranthene 6fold, phenanthrene 12fold less) Due to their hydrophobicity and strong adsorption onto organic soil compounds the bioavailabiltity of PAHs is influenced by amount and nature of humic substances.

REFERENCES

Angle, J.S., McGrath, S.P., Chaudri, A.M., Chaney, R.L., Giller, K.E. (1993) Inoculation effects on legumes grown in soil previously treated with sewage sludge, *Soil Biol Biochem* 25, 575-580

Neumann, H., Bode-Kirchhoff, A., Madeheim, A., Wetzel, A. (in press) Toxicity testing of heavy metals with the *Rhizobium*-Legume Symbiosis with high sensitivity to cadmium and arsenic compounds

Effects of atrazine on maize litter decomposition and litter-bag microarthropods colonization in an experimental maize field

J. Cortet & N. Poinsot-Balaguer

Laboratoire de Biosystématique et Ecologie Méditerranéenne. Université de Provence, Centre Saint Jérôme. 13397 Marseille Cedex 20. France

Keywords : soil fauna, field experiment, pesticides, sampling techniques, biodegradation, ecological effects, agriculture.

Introduction

Soil ecotoxicology must develop the standardized field experiments, to evaluate the biodiversity and quality of soils, particularly in agroecosystems.
To achieve this goal, alternative sampling techniques must be tested.
In this study, we propose using the litter-bag method (Crossley & Hoglund, 1962), to evaluate the effects of atrazine herbicides on microarthropod colonization and maize litter decomposition.

Material and methods

One hundred bags each containing 3.5 g. of maize leaves were placed in an experimental maize field, at La Côte Saint André (Isère, France), in two different plots (control and treated) on January 1996. The two plots had been treated with atrazine for many years, however in June 1996, atrazine was sprayed (0.8 Kg/ha) only over the treated area.
To evaluate the direct effects of atrazine, adventive plants were eliminated by hand in the two plots, but no other chemical herbicides were used. Eight samples were collected every month, from each plot, from February 1996 to February 1997.
The two areas were compared, based on mesofauna densities, collembola diversities, collembola evenness (Shannon index) and litter-mass losses using Mann-Whitney tests. Furthermore, six different regression models were applied to litter-mass data.

Results

A stimulative effect of atrazine on mite densities with significant differences between control and treated areas was observed two months after treatment. Furthermore, collembola diversities and evenness were higher in the treated area (figure 1), and some species, such as *Lepidocyrtus lanuginosus* showed very different patterns
On the other hand, maize decomposition was lower and the tested models always showed a lower correlation in the treated plot than in the control area.

Discussion

Atrazine seems to have a stimulative effect on microarthropod populations, but this « positive » reaction could be due to a high degree of disturbance in the lower levels at the ecosystem (Ramade, 1992).
In fact, atrazine could modify the food resources of mesofauna. It is well known that some fungi such as Aspergillus fumigatus, Rhyzopus stolonifer or Phanerochaete chrysosporium, use atrazine as an energy source (Kaufman & Blake, 1970 ; Mougin et al, 1994). Thus mesofauna could signal micro-organism disturbance, and constitute excellent ecological bioindicators of effects (Texier et al, 1997).

The litter-bag method measures the dynamics of microarthropod colonization. This method consequently compares their colonization preferences, rather than community organisation in the soils. This method could be used in soils which have previously been treated with pesticides for many years, and where micro-organism and microarthropod selection processes make it impossible to locate a genuine control area within the experimental site.

References

Crossley, D.A. and Hoglund Jr, M.P. (1962) A litter-bag method for the study of microarthropods inhabiting leaf litter, *Ecology*, 43 (3), 571-573.

Kaufman, D.D. and Blake, J. (1970) Degradation of atrazine by soil fungi, *Soil Biol. Biochem.*, 2, 73-80.

Mougin, C., Laugero, C., Asther, M.I., Bubroca J., Frasse, P. and Asther, M.A. (1994) Biotransformation of the herbicide atrazine by the white rot fungus *Phanerochate Chrysosporium*, *Appl. Environ. Microbiol.*, 60, 705-708.

Ramade, F. (1992) *Précis d'Ecotoxicologie*, Masson, Paris.

Texier, C., Cortet, J., Gomot, A. and Cluzeau, D. (1997) *La faune, indicateur de la qualité des sols*. Données et Références. Ademe publishers, Paris.

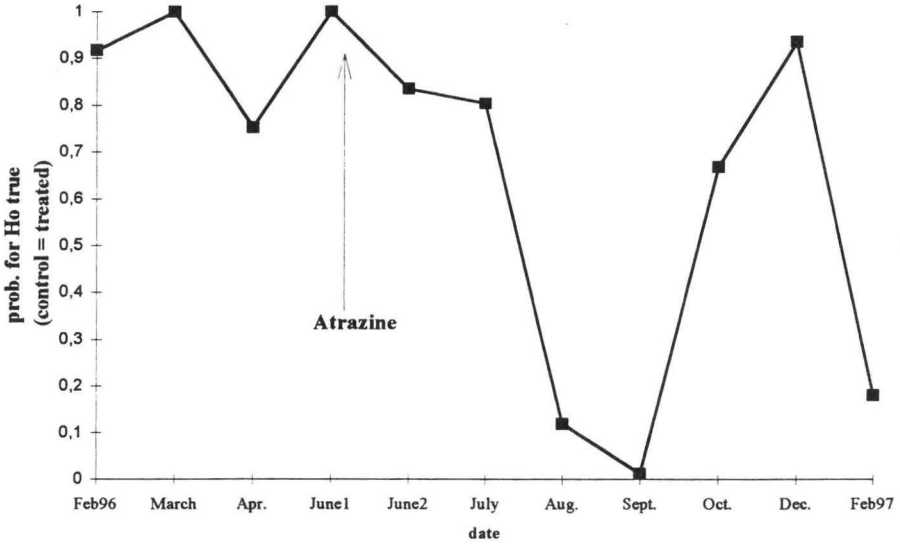


Figure 1 : Differences between control and treated areas on Collembola populations evenness (test of Mann-Whitney).

VLIER-HUMAAN: A HUMAN EXPOSURE MODEL EMBEDDED IN FLEMISH LEGISLATION

P.J. Smit and D.G. Goldsborough

Van Hall Instituut, PO Box 17, 9700 AA Groningen, The Netherlands

Keywords: Risk assessment, computer model, exposure model, human health risk, legislation, knowledge transfer, authorities' role

VLIER-HUMAAN is an user-friendly computer model, originally based on ECETOC-publications with respect to risk assessment, but specially modified for use in daily practice in Flanders, Belgium. These modifications were carried out to ensure that the model matches the Flemish approach to human exposure assessment which is embedded in their legislation concerning soil remediation. This legislation, the Soil Remediation Decree, came into force in 1995 (OVAM, 1995). This decree and the related soil remediation regulation, VLAREBO, state that all activities as part of the soil remediation procedure must take place under the supervision of a certified soil remediation expert (OVAM, 1996a). A soil remediation expert is certified by the responsible authority, the Public Waste Agency of Flanders (OVAM), if he or she complies with certain conditions. One of these conditions is that the expert must use a risk assessment model that has been approved by OVAM, e.g. VLIER-HUMAAN, and that he or she is able to use this model and interpret the results.

The assessment of the risks is part of the descriptive soil examination, one of the steps of the soil remediation procedure. This examination is conducted in order to establish the seriousness of the soil contamination. OVAM only issues a compliance certificate, if the study satisfies the terms of the decree.

VLIER-HUMAAN was developed within the RISC-framework (Smit and Goldsborough, 1994). Software developed within this framework offers users facilities that ensure that the assessment of risks is transparent and reproducible. Parameter value changes must be justified and these changes, together with their justifications, are amongst others included in the results, in a so-called Report. This Report feature facilitates OVAM with a tool to evaluate the results of studies carried out by certified experts. All background information on the risk assessment procedure is present in the model, providing the user with knowledge that supports producing transparent and reproducible risk assessments.

The methodology developed in Flanders for assessing the risks of actual cases of soil contamination is a balance between a tight straitjacket and complete freedom (OVAM, 1996b). Some parameters are fixed, and can not be changed, e.g. the temperature of the soil. A number of parameters only vary with the selected type of land use, e.g. selecting residential land use instead of agricultural land use will effect the fixed parameter value of the amount of soil ingested. The user can not alter these parameter values directly. On the other hand site specific values of parameters must be used (e.g. organic matter content) when available. The user can also define his own type of land use, but it must be based on the existing land use types.

This balance can also be recognised in VLIER-HUMAAN, and this stresses the importance of the accessibility and quality of the presentation of the knowledge; it has to be absolutely clear when the user is not allowed to change parameters, when the change of parameters is recommended or when the change is required.

With the development of VLIER-HUMAAN a risk assessment tool suitable for Flemish legislation has come available for use in the daily soil remediation practice in Flanders. This model is a good example of the possibilities of the open concept of the RISC-framework which allows for the development of tailor made versions of human exposure models for specific situations or countries.

References

OVAM (1995) *Decreet van 22 februari 1995 betreffende de bodemsanering*, De Openbare Afvalstoffenmaatschappij voor het Vlaamse Gewest, Mechelen, D/1995/5024/27

OVAM (1996a) *Vlaams reglement betreffende de bodemsanering - VLAREBO*, De Openbare Afvalstoffenmaatschappij voor het Vlaamse Gewest, Mechelen, D/1996/5024/5

OVAM (1996b) *Basisinformatie voor risico-evaluaties*, De Openbare Afvalstoffenmaatschappij voor het Vlaamse Gewest, Mechelen, D/1996/5024/19

Smit, P. and Goldsborough, D. (1994) *RISC: meer dan de som der delen*, Van Hall Instituut, Groningen, Serie rapporten RISC94/01

TOXICITY OF TRANSURANIC ELEMENTS TESTED ON EARTHWORMS

A.G. Viktorov

Institute of Ecology and Evolution, Russian Academy of Science; Leninsky Prospect 33, Moscow, 117071, Russia.

Key words: soil fauna, radionuclides, earthworms.

The earthworms used in the present experiments were sexually mature *Aporrectodea caliginosa* Savigny (1826). To study the accumulation of ^{239}Pu and ^{241}Am 150 earthworms were placed in each of three pots with the soil containing 3.5 MBq/kg of ^{239}Pu and 1.7 MBq/kg of ^{241}Am artificially applied as Plutonium and Americium nitrates. To study the accumulation of ^{239}Np and ^{244}Cm, 100 earthworms were placed in each of three pots with soil containing 1.3 MBq/kg ^{239}Np and 0.22 MBq/kg ^{244}Cm artificially applied as Neptunium and Curium nitrates.

The intensive accumulation of ^{239}Pu into earthworm body tissues proceeds for seven days. During that time the earthworms practically accumulate the maximum amount of ^{239}Pu (12 kBq/kg). During the last days of the experiment some decrease in the concentration of the radionuclide to 2.9 kBq/kg dry weight of earthworms was recorded. Concurrently, ^{239}Pu accumulated in the casts where 10- to 12-fold the body concentration of the radionuclide was measured.

^{241}Am began to accumulate in earthworm bodies only on the second day after the animals were placed in the radionuclide-polluted soil. The concentration of nuclide in the earthworm reached its maximum by the seventh day and was 6.5 kBq/kg, which was half that of ^{239}Pu for the same period. After the maximum concentration was reached in the earthworm's body (on the seventh day), it decreased a little during the following days of the experiment.

Comparison of the behavior of the two elements reveals similarity of accumulation of ^{239}Pu and ^{241}Am by earthworms living in chernozem soil. At the same time, some difference in the accumulation of these radionuclides were observed in casts, where the concentration of ^{239}Pu exceeds that of ^{241}Am several times.

Based on the experimental data, the concentration ratio of ^{239}Pu and ^{241}Am by earthworms were calculated to range within 0.0003-0.0004. In fact, it means that the elements are incorporated inbiological tissues in small quantities. A gradual increase in the concentration ratio of ^{239}Pu and ^{241}Am is attained on the tenth day of the exposure to the polluted soil.

It took 3 days for of ^{239}Np to accumulate in earthworm's body. Over that period earthworms accumulate the maximum quantity of ^{239}Np- 510 Bq/g of dry weight. In the following days of the experiment some decline of radionuclide concentration to 310 Bk/kg was recorded. Concurrently, an increase in the content of ^{239}Np took place in the intestinal tract, where the radionuclide concentration on the 20-th day was three times as high as that in the body. The latter is associated with a decline of the deposition of ^{239}Np in the tissues. The concentration of ^{239}Np showed a steady increase by day 20.

Contaminated Soil '98, Thomas Telford, London, 1998, 1047–1048

Based on the data obtained from the present experiment, the concentration ratio of ^{239}Np by earthworms range between 0.7 and 0.39, indicating that this element is incorporated in tissues at only at half the rate of ^{90}Sr. For ^{90}Sr concentration ratio of 0.52 - 0.67 were obtained, according to the soil type. The maximum accumulation of ^{239}Np in earthworms occurred within the first 3 days of exposure. During subsequent days the accumulation of ^{239}Np by earthworms in a leached chernozem was essentially similar to that of ^{90}Sr [Krivolutzky *et al,* 1992].

After the first 12 hours of exposure to the soil contaminated with ^{244}Cm earthworms became less active. After 24 hours the entire population was eliminated, the bodies reduced to mucoid knots and strands. Concentration of ^{244}Cm in the given experiment was lower, as compared to other radionuclides. Radiation alone couldn't be responsible for the death of the earthworms [Viktorov, 1995]. This is supported by the results of the experiment in which higher concentrations of ^{239}Pu, ^{241}Am, ^{239}Np were involved [Krivolutzky *et al,* 1992]. Therefore, in the experiments on ^{244}Cm a chemical factor becomes important. The ^{244}Cm concentration of 220 kBq/kg dry soil, is shown to be highly toxic for earthworms.

A long-term dynamics of the ^{239}Pu and ^{241}Am accumulation by earthworms has been first estimated in experiments with earthworms dwelling under conditions of soil radioactive pollution, and concentration ratio of ^{239}Pu and ^{241}Am were calculated for those elements. However, Americium has a stronger affinity to inorganic part of the soil and hence is concentrated in earthworms in smaller amounts.

The concentration of ^{239}Pu in earthworm casts during the entire observation period was two to seven times higher than the body radioactivity, but in the experiments with ^{241}Am the former rarely exceeded he latter.

However, during the entire period of observations, the concentrations of ^{239}Pu, ^{241}Am, ^{239}Np in earthworm body and casts did not exceed their concentration in the soil. This is probably due to the fact that ^{239}Pu, ^{241}Am and ^{239}Np are strongly bound to soilcomplexes and do not readily pass into a soluble state.

REFERENCES

1. Krivolutzky, D.A., T.L. Kozhevnikova, V.Z. Martjushov and G.I. Antonenko. (1992) Effects of transuranic (^{239}Pu, ^{239}Np, ^{241}Am) on soil fauna, *Biology and Fertility of Soils 213: 79 - 84.*

2. Viktorov, A.G. (1995) Differential reactions of lumbricids to radioactive pollution in various biotopes of Chernobyl region, in W.J. van den Brink *et al.* eds., Contaminated Soil'95. Kluwer Academic Publishers, Netherlands, pp. 265 - 266.

EVALUATION OF THE PREDICTIVE CAPABILITY OF MODELS OF EXPOSURE TO SOIL CONTAMINANTS

J. Kissel[1], A. Wawrukiewicz[2], S. Bartell[3] and J. Shirai[1]

[1]Department of Environmental Health, University of Washington, Seattle, WA 98195-7234, USA
[2]U.S. EPA Region 10, 1200 6th Avenue, Seattle, WA 98101, USA
[3]Consortium for Risk Evaluation with Stakeholder Participation (CRESP), University of Washington, 4225 Roosevelt Way NE, #100, Seattle, WA 98105-6099, USA

Keywords: Contaminated soil, exposure, exposure pathway, human health risk, models, risk assessment, soil clean-up criteria

Clean-up decisions regarding contaminated soils are typically based on rudimentary exposure assessments. In the U.S., these assessments have historically employed simple deterministic models of potential pathways. Concern over the cost of clean-ups has fostered criticism of regulatory models as excessively cautious. In particular, inclusion of high-end estimates of multiple exposure factors can be expected to lead to compounded conservatism. The primary remedy for this problem involves use of distributed parameters and characterization of uncertainty and variability in expected exposures. While stochastic description of exposure factors is intellectually much more appealing than traditional deterministic methods, implementation is hindered by the same lack of information that led to the use of conservative point estimates in the past. Validation of probabilistic models is therefore appropriate, but in practice has seldom been attempted. This is in part due to a lack of data against which model predictions can be tested. Deliberate exposure of human subjects in a manner adequate to test the models in question is problematical. However, some data are available as a result of post hoc biomonitoring conducted at sites where exposures due to soil contamination were suspected.

The approach taken here is to develop case studies for which sufficient environmental and biomonitoring data exist to permit evaluation of regulatory model perfomance. In the U.S., cases are more readily available for inorganic than organic soil contaminants. Contamination of soil by either lead or arsenic is relatively common as a consequence of mining and smelting activities. However, the widespread use of lead-based paint and the complicated pharmacokinetics of lead often make interpretation of lead biomonitoring data very difficult. In contrast, arsenic displays relatively simple pharmacokinetics. Organic contaminants for which appropriate data are most likely to be found include pesticides and PCBs.

Results from an arsenic case study are presented in Figure 1. Biomonitoring data from two separate studies with 22 and 73 two to six-year-old subjects are available (labeled Pathways and TPCHD in Figure 1, respectively). The subjects lived in close proximity to a smelter. The data were collected approximately two years apart and urinary arsenic levels declined substantially over that period. Although the smelter ceased operation in the interim, the observed changes in exposure are too large to be explained directly by observed changes in air concentrations. Because the urinary values shown are also corrected for background (dietary) exposure, they should represent the effect of local environmental contamination. However, available data do not reveal a reduction in arsenic concentrations in soil following shutdown of the smelter. It appears that behavioral changes may account for a substantial portion of the observed decrease.

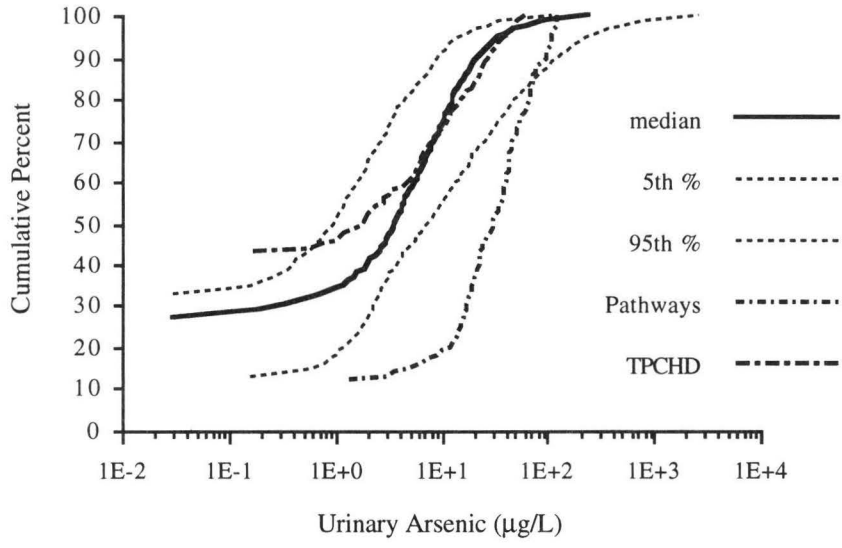


Figure 1. Two-dimensional Monte Carlo prediction of children's urinary arsenic levels and results of two biomonitoring studies conducted at a former smelter site in the State of Washington, USA.

A urinary arsenic distribution generated using two-dimensional Monte Carlo analysis is also displayed in Figure 1. Exposure pathways considered include ingestion, inhalation, and dermal absorption of arsenic in soil and dust. Input parameters can be selected to produce results similar to either set of biomonitoring data, but not both simultaneously. Since regulatory decisions must be made without the benefit of hindsight, this finding raises important questions. In addition, input values required to produce predictions similar to observed results cannot be considered conventional. Use of probabilistic estimates of relevant exposure factors available in the literature does not ensure that actual exposures will not be substantially under predicted.

A second case involves observed changes in blood lead levels in 149 pre-school children following soil lead abatement. Results suggest relatively low exposures to soil lead. If estimated soil ingestion rates derived from this case are applied to the arsenic case introduced above, actual body burdens are greatly underestimated.

Findings from these and other cases reflect the inherent difficulty of predicting exposures that are heavily dependent upon human behavior. Caution is warranted in assuming that distributions of exposure factors that are applicable across temporal, geographical, and social boundaries can be obtained.

Funding for this work was provided by the U.S. Environmental Protection Agency (USEPA) through Cooperative Agreements R819052-01-0 and CR824065-01-0 and by the U.S. Department of Energy (USDOE) via the Consortium for Risk Evaluation with Stakeholder Participation (DE-FCO1-95EW55084). However, this document has not been reviewed by USEPA or USDOE and should not be assumed to represent agency or department views.

REFERENCES (see http://weber.u.washington.edu/~jkspage/)

NEW BIOLOGICAL AND ECOTOXICOLOGICAL METHODS TO SUPPORT RISK ASSESSMENT AND SOIL REMEDIATION

Katalin Gruiz, Mónika Molnár, Tünde Szakács and Tünde Bagó
Technical University of Budapest, St. Gellért Sq. 4. Budapest, 1111, Hungary,

Keywords: remediation, bioremediation, bioassay, ecotoxicology, risk assessment, heavy metals, hydrocarbon, PAH

Biological and ecotoxicological characterisation of contaminated soil gives necessary information in all phases of the remediation from planning through the remediation procedure until the control and monitoring of the remedied site.
The **transport and biodegradation** of the contaminant or the mixture of contaminants highly influence the hazard and the risk. Physical, chemical and hydrogeological data accomplished by biological and ecotoxicological results are necessary to assess the site specific environmental and human health risk of contamination. The quantified risk helps the decision making; priorization, the selection of a physico-chemical, biological, often a complex *in situ* or *ex situ* remediation technology.
Biological investigations play role in determining toxicity and biodegradation of the contaminant and in the characterisation of the contaminated soil and its microflora. The **ecotoxicological effect** of the contaminated soil is to be measured by acute- and chronic toxicity tests. The **biodegradation** of the contaminant depends on the degradative activity of the soil microflora. The adaptation and/or the adaptive potential of the microflora of the contaminated soil has basic importance when a biotechnology is to be applied. The time requirement of the technology depends on the biodegradability and the bioavailability of the contamination. Biochemical pathway and metabolites may cause changes in the toxicity during bioremediation. Determination of the optimal technological parameters like rate of aeration, temperature, nutrient supply, also requires biological investigations (1,2).
The **bioavailability** of the contaminant may be estimated by comparison of the chemical analytical data and the biological and ecotoxicological results. Adsorption capacity of the soil and partition of the contaminant specifies leaching, desorption and volatilisation. The partition of toxicity between the solid, the water and the gaseous fractions of the soil results in a risk on ground water or on air. Toxicity measurements help in the assessment of risk of mixed and even not identified contaminants.
The mobilisation or immobilisation of the contaminants may change during the bioremediation. Due to microbial activity desorption, leaching and solubility often increase. Biodegradability of the components of contaminant mixtures may decrease during remediation, because of selective biodegradation. Changes in the toxicity and bioavailability may also occur during application of a cleanup technology. Applying of *in situ* technologies continuous risk assessment is necessary. The acceptable **environmental risk** of the remedied site should be based on the results of ecotoxicity tests.

Heavy metal contamination was characterised by the following biological and toxicological methods: *Vibrio fischeri* luminescence inhibition, *Bacillus subtilis* growth inhibition, *Azotobacter agile* and *Pseudomonas fluorescens* dehydrogenase inhibition, *Sinapis alba* (white mustard), *Raphanus sativus* (reddish) and *Triticum sativum* (wheat) germination, root and shoot elongation tests. Solid phase test is accompanied by direct contact with soil. In the water phase test the aqueous solutes or the equilibrium pore water is used. Direct contact tests were developed by the authors by the modification of ISO, DIN or Hungarian Standard methods (3,4,5,6). The advantage of the direct contact tests (whole soil) is, that their result includes the effects of the possible interactions between contaminated media and testorganism. This kind of interactive laboratory bioassays resemble the microcosm tests. Direct contact tests were developed for solid phase soil by *Bacillus subtilis*, by plants, and by *Collembola*. The other bacterial biotests work with slurry phase soil (7,8).
Binding and bioavailability of heavy metals were characterised by comparing the toxicity of aqueous solution and that of in absorbed form onto soil.

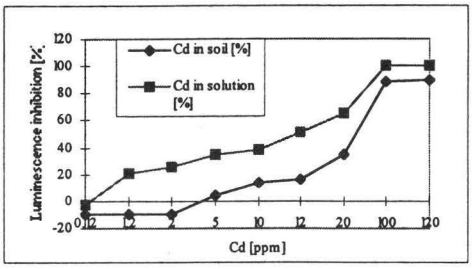


Figure 1. *Vibrio fisheri* luminescence inhibition of Cd

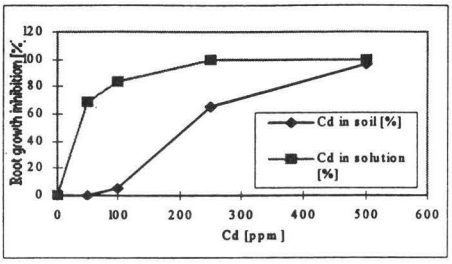


Figure 2. *Sinapis alba* root growth inhibition of Cd

Toxicity of Cd dilution series in water is higher, than the one absorbed on soil. The area between the curves of solute and whole soil is proportional with the absorption capacity of the soil and the strength of the binding of the contaminant to the soil, The size of this area may well characterise the environmental fate and binding capacity of the soil.

Hydrocarbon mixtures in the soil and their remediation may be investigated by biological and toxicological methods. The biological activity depends on the living cell number (plating) and on the number of the oil-degrading cells (statistical MPN method). By measuring of the total **ATP content** of the soil-microflora the mistakes of the methods based on isolated cultivation could be eliminated. The aithors succeded in developing the ATP analysis of soil by measuring luminescence.

The **activity** of the soil-living microflora may also be characterised by the **respiration**: CO_2 production and/or O_2 consumption. Using a self-made mini-reactor a rapid method was elaborated for measuring respiration. One-day and one-week experiments were suitable to indicate and follow the adaptation, to quantify biodegrading activity and its stimulation and to determine the technological parameters, like aeration rate, temperature or application of additives.

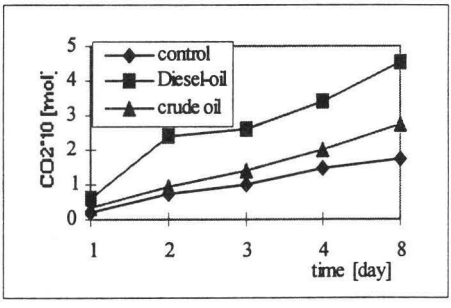


Figure 3. CO_2 production of soils contaminated with different hydrocarbons

For **ecotoxicological testing** of hydrocarbon contaminated soil *Vibrio fisheri*, direct contact luminescence inhibition, *Azotobacter agile* and *Pseudomonas fluorescens* direct contact dehydrogenase enzyme activity and *Sinapis alba*, direct contact, germination, root and shoot elongation and *Folsomia candida*, direct contact growth tests were used.

References

1. Gruiz, K. and Kriston, É.: In-situ Bioremediation of Hydrocarbon in Soil - J. of Soil Contamination **4** (2) 163-173, 1995
2. Gruiz, K., Murányi, A., Molnár, M. and Horváth, B.: Risk Assessment of Heavy Metal Contamination in Danube Sediment - J. of Water Sci. and Technol., in press, 1998
3. DIN 38412 Inhibitory effect of waste water on *Ph. phosphoreum* - German Standard, 1991
4. MSZ 21470-88 *Pseudomonas fluorescens* soil toxicity test - Hungarian Standard, 1993
5. MSZ 21978/30-88 Investigation of hazardous waste; *Azotobacter agile* test - Hung. St., 1989
6. MSZ 22902-4 Water toxicological test; Plant seedling test - Hungarian Standard, 1991
7. Horváth, B., Gruiz, K. and Sára, B.: Ecotoxicological testing of soil by four bacterial biotests Toxicological and Environmental Chemistry **58**, 223-235, 1996
8. Horváth, B. and Gruiz, K.: Impacts of metallyferrous ore mining in Gyöngyösoroszi, Hungary - A case study - The Science of the Total Environment, **184**, 215-227, 1996

CONTAMINATED SOIL '98

Theme E:
Remediation and treatment technologies, research and development and proven technologies

MONITORING OF CLAY-TYPE SURFACE BARRIER ON DUMP SITES

Alex Brandelik and Christof Huebner
Inst. für Meteorologie und Klimaforschung, Forschungszentrum Karlsruhe GmbH / Universität Karlsruhe, Postfach 3640, D-76021 Karlsruhe, Germany

Keywords: Soil moisture, Barrier, Waste disposal, Clay liner, Dump site monitoring

The disposal of toxic wastes threatens aquifers and atmosphere world wide. Due to stability, plasticity and low water and gas conductivity clay-type mineral layers are used for bottom and surface barriers in containment constructions. A disadvantageous property of clay is shrinking and swelling as a result of changing water content. The consequences are irreversible cracks and enhanced mobility of water and gas. In order to prevent this case the primary task of a monitor system is the measurement of the hydraulic conductivity of the clay liner. The direct determination of this parameter is possible with lysimeters only. They are expensive and limited to small areas. The most commonly used indirect parameters are water content and density. Soil-physical and soil-mechanical models relate these parameters to the hydraulic and gas conductivity. Like several authors and promoters we also recommend to monitor the clay moisture as a reliable and sufficient indirect alert parameter to warn against possible leaching.
A monitoring system has to measure accurately, economically and long-term on a large area. Our patented Moisture Sensor For Extended Areas fulfills these demands.
Device and Method: Moisture sensitive radiofrequency cables are buried in the clay mineral liner in the test field of the Municipal Waste Disposal Karlsruhe-West (Fig.1).

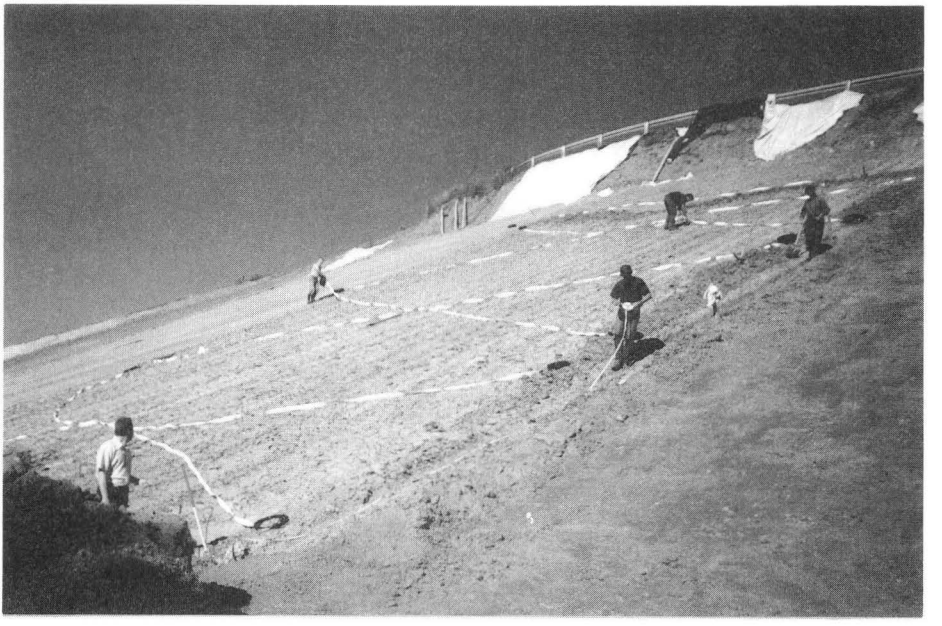


Figure 1, The view of the dump site during the cable sensor construction

Contaminated Soil '98, Thomas Telford, London, 1998, 1055–1056

In order to sense a large area and to achieve a surface resolution the cables are cross-led. Additional cables are buried under and above the clay liner for further studies, too. Cables and connectors are constructed for a life time longer than 30 years. Redundant measurements of the complex signal propagation along the cable sections in time and frequency domains and the cross-talk between two cables provide the dielectric coefficients of the moist clay in the neighborhoods of the cables. The diel. coefficients will be converted in relative water contents. By the help of an absolute measurement (gravimetric measurement of the control authority, or by a cryo moisture sensor Brandelik (1997)) the calibration in absolute water content can complete the moisture mapping.

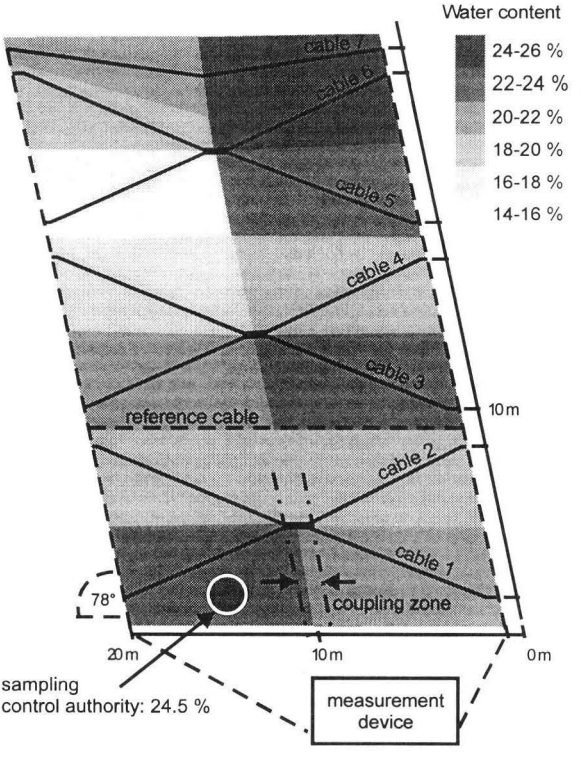


Figure 2 Moisture distribution map

Results: This system is non-destructive and allows long-term monitoring. It is designed to operate for longer than 20 years. Corresponding to Fig. 2 a 2 % mass related water content change can be localized with a distance accuracy of approx. 4 m. (The volume related relative accuracy is better than $\pm$ 0.2 %.) The result of each field part is fetched from a sufficient large representative area of approx. 45 m^2. Even if the method is a relative one, the comparison between our measurement and that of the control authority is very good. The average water content measured on the whole field is 20.6 $\pm$ 1 % without the above mentioned absolute calibration. On the same place the control authority measured a mean value of 19.9 $\pm$ 1 %.

This is a good proof and evidence for the correctness of the applied relation between dielectric constant and water content. A simple share setting can cut the cable without any consequence to the further operation. In this case the place of the setting will be localized also. Only multiple cuttings can destroy a part of a cable section. Moisture differences are remarkable between the sections.

Costs: Acquisition, installation and the first year operation cost \$ 4,- / m^2.

Sponsor: Projekt Wasser - Abfall - Boden (Water - Waste - Soil) of the Government Baden - Württemberg.

Reference: Brandelik, A., et al.(1997) Zerstörungsfreie In-situ Messung der Feuchte und Dichteänderung von mineralischen Deponieabdichtungen , *Müll und Abfall 1, 97, 36-41*

REMEDIATION OF AN INDUSTRIAL SITE CONTAMINATED WITH ELEMENTARY WHITE PHOSPHOROUS AT BITTERFELD, SACHSEN-ANHALT, GERMANY - EXPLORATION AND REALIZATION

U. Neef[1], G. Kotte[2], R. Düresch[3], A. Boehringer[4], P. Böhme[4], V. Bergmann[3]

[1] Bitterfelder Vermögensverwaltung Chemie GmbH, Zörbiger Str., D - 06749 Bitterfeld
[2] TÜV Ostdeutschland GmbH, Köthener Str. 33, D - 06118 Halle/S.
[3] BSB Bodensanierungsges. Bitterfeld mbH, Parsevalstr. 14a, D - 06749 Bitterfeld
[4] WOSAB Sanierungsberatung GmbH, Thälmannstr. 13a, D - 06766 Wolfen

Key words: Phosphorous, contaminated site, excavation, analytical methods, chemical treatment, remediation, reuse

SUMMARY: In order to remediate an old chemical site prior to redevelopment, some 4900 tonnes of phosphorous-bearing material had to be removed. Elementary white phosphorous ignites spontaneously and is thus regarded as a serious environmental hazard. The excavation was completed between August 1996 and April 1997. The phosphorous-bearing soil and building rubble was processed offsite with a newly developed technique (patents pending) using hydrogen-peroxide to get a mineralized disposable material.

The production of elementary white phosphorous in Bitterfeld as a primary product for (among other things) pesticides, ammunition, softeners and matches started in 1900 and continued with interruptions until 1992. Phosphorous was extracted from apatite using heat in electric furnaces. The generated phosphorous gas was then filtered and cooled to get white phosphorous. The filter cakes and other residues were disposed of as warm sludge into basins nearby. The production site (including furnaces, filters, washers, coolers and disposal basins) had a size of approx. 110 by 70 metres.

Elementary white phosphorous is chemically very active. It melts at 41°C. As a liquid it is less viscous than water; enabling it to fill any subsurface hollows and fissures before solidifying. Spontaneous ignition in contact with oxygen can already start at room temperatures; with other forms of energy (e.g. sunlight) supporting this reaction. The combustion can cause deep burns on the skin. This chemical reaction is an oxidation to phosphorous pentoxide and phosphorous acid, both forming a white toxic vapour. These properties mean a fire hazard at any time.

The remediation was therefore funded by the Federal Agency for Unification Tasks (BvS), the former Treuhand Privatisation Agency, and the state of Sachsen-Anhalt as part of actions to eliminate environmental hazards at the Bitterfeld Chemistry Complex.

Explorations of the site in 1994 revealed approx. 1700 tonnes of phosphorous-contaminated soil above the groundwater table. Elementary white phosphorous was found in bricked-up basins, in the sewers and in the neighbouring soil. With a dense grid of boreholes (53 on 8.000 sqm) about 25 % of the area was detected as phosphorous-bearing, whereas other parts were not contaminated. However, lots of foundations (some of them more than a meter thick) and other drilling barriers prevented a complete exposure of the site.

In the field the property of self-ignition was used for a quick analytical method. Put on a hot-plate, the sample was classified in five categories between no reaction (< 0,1 % phosphorous) and explosive fire (> 10 % phosphorous) according to the intensity of the vapour and/or fire („fire test"). This easy testing allowed a large number of analyses. The results could be plotted in maps showing lateral and vertical phosphorous dissemination.

Because no remedial threshold value is known for elementary phosphorous from the literature, intensive discussions between the proprietor, the developer and the authorities were needed to determine the remediation targets, in order to achieve both a complete elimination of hazards and a practicable realization on site. As a result, the remedial threshold was pinpointed at a positive fire test (i.e. 0,1 % phosphorous) for all material above the groundwater table. No potential hazard was seen under water.

On site, an independent engineer carried out the fire test and controlled the separation between phosphorous and non-phosphorous material. By all participants this was regarded as the most effective way to minimize the material requiring the expensive special phosphorous decontamination and to get verified mass balances for the account.

The remediation works started in August 1996. According to material and its phosphorous content, excavators of different sizes, pneumatic hammers, spade and shovel were used. While excavating, fresh cuttings were sprinkled. During breaks they were covered with sand or put under water to minimize the formation of phosphorous vapour or even fire. A sufficient amountof sand and water were required on site, as well as a hotline to the fire brigade. As an additional safety measure, a fire-watch was installed around the clock. The excavation of approx. 50000 tonnes (of which some 4900 tonnes contained phosphorous) was completed in April 1997, due to an interruption by 2 months of frost. The main reasons for the discrepancy between the earlier estimate and the actual results were: (a) the production site was larger than shown on the plans, (b) additional basins and sewers were found, containing massive phosphorous, (c) the building rubble, originally thought not to contain phosphorous, was also contaminated and (d) the estimates for the areas covered with foundations proved too low due to unavailable exploration data.

Whereas the phosphorous-free material could be carried off to a sanitary landfill directly, phosphorous-bearing material was deposited under water in barrels and carried off-site for further processing. This processing method for material containing up to 10% phosphorous included the following steps: (a) separation of phosphorous-free fines, (b) oxidation of the residue with hydrogen-peroxide (using copper as a catalyst) into phosphorous acid, (c) neutralization with lime to phosphate and (d) dewatering to get a solid sludge, which could be disposed of on a sanitary landfill. Some organical contaminants found in the soil were also destroyed by the hydrogen-peroxide and therefore caused no problem for deposition. A patent for this processing method is pending. Material containing more than 10 % phosphorous was incinerated.

The specific costs for excavating, processing and disposal of phorphorous-bearing material reached about DM 2300 per ton.

To the knowledge of the authors, it was the first completed remediation of a contamination with elementary white phosphorous in the world. On the site, a new production complex of Akzo Nobel Chemicals was built and went into operation.

RECLAMATION OF POLLUTED WET SOILS BY SOLVENT EXTRACTION

A. Nardella and R. Sisto
Eniricerche, Via E. Ramarini 32, 00016 Monterotondo (RM), ITALY

Key words: chlorinated hydrocarbons, contaminated soil, extraction, solvents

Eniricerche solvent extraction system to treat contaminated soils is based on the use of a mixture of two environmental friendly solvents: acetone and ethyl acetate. Mixture composition is chosen case by case as a function of soil water content in order to get as intimate soil-solvent contact as possible, according to a proprietary method [1]. The ternary phase diagram of the system ethyl acetate - acetone - water is shown in figure 1. The proper ethyl acetate / acetone ratio is chosen in order to obtain a single phase with the water present in the soil using the minimum amount of acetone. In such way the good solvent properties of ethyl acetate and of acetone are added to an intimate and very effective soil-solvent contact.

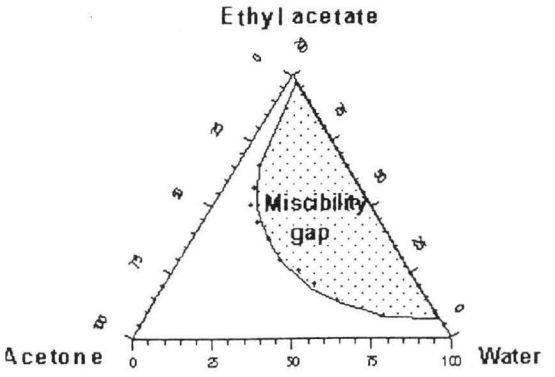


Figure 1

Experimentals have been carried out using a bench scale equipment, with a treating capacity of 15 ÷ 20 kg of soil per batch. Treatment tests were successfully performed using a sandy soil, containing 20% of water, contaminated with chlorinated aromatic and aliphatic hydrocarbons.The contaminated soil, excluded materials larger than 10 cm, underwent a mixing/extraction step, followed by soil/solvent

separation performed by means of a vibrating screen. Exhausted solvent was recovered by evaporation, while clean soil was finally dried to recover the imbibition solvent. Extraction and separation steps have been performed at room temperature and under a slight nitrogen pressure in order to avoid the formation of flamable air/vapor mixtures. Results are summarized in table 1.

	untreated soil mg/kg	treated soil mg/kg
Hexachloroethane	1156	< 0.5
1,2,4Trichlorobenzene	309	0.62
1,2,3 Trichlorobenzene	37	<0.5
Hexachlorobutadiene	3154	1.83
2,4,5 Trichlorotoluene	445	1.9
1,2,3,5 Tetrachlorobenzene + 1,2,4,5 Tetrachlorobenzene	154	<0.5
1,2,3,4 Tetrachlorobenzene	254	1.05
Pentachlorobenzene	187	4.06
Hexachlorobenzene	181	4.97
Total	5877	14.4

Table 1: results of soil treatment

Recently, Eniricerche system proved to effectively treat a soil coming from a Manifactured Gas Plant, containing more than 2000 mg/Kg polynuclear aromatic hydrocarbons, and another one characterized by the presence of non volatile chlorinated hydrocarbons, included polychlorobiphenyls.

1. Nardella,A., Sisto,R., Reclamation of polluted wet soils, US patent 5,585,002 (17/12/96).

INVESTIGATION AND OPERATION OF COMBINED TREATMENT AND CONTAINMENT SYSTEMS, 'ACTIVE CONTAINMENT', CONCEPTS AND CASE HISTORIES

S.A. Jefferis[1] and V. Forster[2]

[1]Golder Associates, 54 Moorbridge Road, Maidenhead, Berkshire, SL6 8BN, England
[2]The Environment Agency, Steel House, Tothill St., London SW1H 9NF, England

Key words: groundwater remediation, in-situ remediation, remediation concept

Golder Associates has been undertaking a review of the theory and practice of combined treatment and containment systems (active containment) for the UK Department of the Environment Transport and Regions (DETR) Contaminated land and Liabilities Branch[1]. This review developed a working definition of active as: 'an active containment is essentially a surface or zone through which a contaminant or contaminated fluid (liquid or gas) can move, and whilst doing so is treated to improve its quality'. It follows from this definition that active containment excludes physical containment with low permeability barriers but may include natural processes occurring in the ground such as intrinsic remediation. It should be noted that although the term active containment is common in the UK for such processes it is not used in North America where terms such as permeable reactive walls may be more common.

Active containment can be distinguished from passive containment by considering the controls on the flux of contaminant, that is the product of flow and concentration. For a barrier the flux is controlled by ensuring that the permeability and hence the flow is low. For an active containment, flux is controlled by controlling concentration. The permeability may be high or low as appropriate to the application.

Technology issues: one of the problems with all forms of passive containment is that they distort the local hydrogeology, therefore measures may be necessary to mitigate the effects, for example, to prevent build-up of water within a contained site. With active containment there is an opportunity to accept or exploit the natural groundwater regime, provided that has been well characterised, and to engineer the contaminant/barrier interaction. In general in any active system there will be two fundamental issues: the physical deployment of the system and the active treatment processes for the contaminants. The physical system may have to fulfil three functions:

- collector: collection of the contaminated fluid, storage to regulate throughput, physical pre-treatment, e.g. separation of liquid, gaseous or non-aqueous phases and homogenisation of the flow through the reactor volume,
- reactor: processing within a reactor or reactor train (chemical, biological, physical),

- distributor: distribution of the treated flow into the downstream area.

These functions may be provided by a Funnel and Gate™ geometry[2] or other systems including in-ground reactors where the flow between collector, reactor and distributor may be piped rather than via natural ground (the first application of active containment in the UK used an in-situ reaction chamber set in a cement-bentonite cut-off wall[3]). Hydrofracture also may be used to introduce active materials and combine the three functions within a single zone[4] (see the poster presentation for case histories). The location of the active zone in relation to any containment is important. For example, better control and performance of the zone may be achieved by locating it inside a containment rather contiguous with a containment wall. In certain site specific cases, the risk management scenario may support the active element being at some distance from the source to take advantage of any intervening intrinsic remediation processes.

Treatment processes: the most widely applied active containment process is the use of iron filings to dechlorinate reductively chlorinated solvents in groundwater and to precipitate/modify redox sensitive species. Other processes have been applied/reported[5] including the use of pillared clays to sorb metals and organics, the use of activated carbon, and processes relating to phosphorus, arsenic, uranium and denitrifcation.

The role of active containment: an active containment may be used either as a source treatment or a pathway control measure depending on issues such as natural decay of the source and the cost-benefit of remediation versus control. Often the most economic application may be as a pathway control mechanism - especially if the contaminant of interest is of moderate to low solubility and so will leach only slowly from the source or will biodegrade in and around the source.

Research needs: Many of the current active technologies are suitable only for a single class of contaminant and technologies need to be developed to treat mixed systems. A full understanding of active containment systems and the development of protocols for their evaluation and prediction of long term performance are needed. As active containment relies on continuing concentration control the costs of monitoring can be significant and economic monitoring technologies are also needed.

This work was funded by the DETR but the views expressed are those of the authors and not necessarily the DETR

1. Golder Associates (1998) *Investigation of combined treatment and containment systems, i.e. Active Containment*, DETR Report EPG 1/6/16.
2. Starr, R.C. and Cherry, J.A. (1994) In-situ remediation of contaminated ground water: the funnel and gate system, *Ground Water, V.32, pp 465-476.*
3. Jefferis, S.A., Norris, G.H. and Thomas, A.O. (1997) Contaminant barriers: from passive containment to reactive treatment zones, *Fourteenth International Conference on Soil Mechanics and Foundation Engineering, Hamburg.*
4. Hocking, G and Wells, S. (1996) Hydraulic fracturing for placement of zero valent iron reaction barriers, *2nd Annual Florida remediation conference.*
5. First International Containment Technology Conference (1997) Florida.

GUIDELINE MONITORING SOIL QUALITY FOR INDUSTRIAL ACTIVITIES

Van Vossen, W.J., Slenders, H.
IWACO, Consultants for Water & Environment, P.O.Box 525, 5201 AM, 's-Hertogenbosch (NL)

Keywords: Industrial sites, guidelines, soil protection, monitoring, soil air, groundwater

1. INTRODUCTION AND OBJECTIVES

In the Netherlands the "Dutch Guidelines for Soil Protection of Industrial Sites" have been recently implemented (January, 1998) by the Ministry of Housing, Spatial planning and Environment. The "Decision Support Model for Soil Protection Strategy of Industrial Sites" is the core this guideline.

This Decision Support Model has to be considered as an instrument which enables private companies and authorities to reach agreement on the soil protection strategy to be followed. In general the soil protection strategy consists of (a combination of) measures which minimize the risk of contamination of soil and groundwater as a result of industrial activities. One of these measures can be monitoring of soil air and groundwater.

Within this scope IWACO has developed a "Guideline Monitoring Soil Quality Industrial Activitities" in assignment for the Ministry of Housing, Spatial Planning and Environment. The objective of this guideline can be formulated as:

> *"Guideline for the design of monitoring systems by which potential spill of contaminants in soil and/or groundwater can be quickly detected in a reliable and efficient way".*

2. STRUCTURE OF THE GUIDELINE

The guideline has been structured by means of the following 4 main parts:

- Investigation & selection of compartment (soil air/groundwater) to be monitored;
- Design of infrasructure & exploitation of monitoring system;
- Construction & realisation of monitoringsystem (piezometers/soil vapour probes);
- Exploitation & maintenance of the monitoringsystem (treshold values, action scheme).

3. RESULTS OF INVESTIGATION

The effectiveness and reliability of a montoringsystem are depending on the quality of the basic-data. These basic-data concern:

company related data:
- kind of industrial activity;
- possibility (risk) that a spill of contaminant will take place;
- the kind of contaminant that can be emitted.

location related data:
- soil profile;

- velocity of groundwater;
- thickness of the unsatured zone;
- soil-chemical behaviour of the contaminant.

These basic-data are the input for the generated decision support models (flow-charts). With regard to the local specific situation of the industrial area, these flow-charts lead the user automatically to the right answers to the following questions, such as:

- Which environmental compartment (soil air and/or groundwatar) is the most suitable to be monitored ?
- Which monitoring techniques (piezometers, soil air probes, drains) and measuring methods (analysing in-situ/off-site/on-site) are suitable ?
- Which distance between source and monitoring-point and which corresponding frequency of monitoring has to be regarded ?

4. DESIGN AND CONDITIONS

From the point of view of soil protection policy, the main conditions are:

- the monitoring points have to be situated as near as possible to the potential source of contamination.
- the chance of detection of a spill must be as high as possible.

Starting from these main conditions, the guideline takes also into account what is feasible in the given circumstances; so the design of a monitoring-system will be based on a combination of the following main criteria:

- the effectiveness of the monitoring system (chance of detection);
- the flexibility of the monitoring system, i.e. the possibility of changing the system as a consequence of results of analyses and field surveys;
- the quality of the monitoring system (controlability);
- the environmental cost-effectiviness, i.e. the costs of monitoring versus the costs of remediation of detected contamination; monitoring near by the emission point means high costs of monitoring and relatively low costs of remediation and vice versa.

5. REALISATION AND EXPLOITATION

The guideline also provides procedures for quality control and quality assurance during construction and management & control of the monitoring system. It concerns:

- the organization (tasks, competencies, responsibilities);
- data management (treshold values, interpretation & presentation of analyses);
- action scheme (flow-chart) in case of exceeded treshold values.

REFERENCES

Van Vossen, W.J., Slenders, H. (1998), Guideline Monitoring Soil Quality Industrial Activities, *IWACO-report, 335.0230, January, 26, 1998.*

SLURRY TRENCH CUT-OFF WALLS: TWO YEARS OF RESULTS FROM THE BG-BRE TEST SITE

P Tedd[1], I R Holton[1], S Wallace[2] and P J Daly[3]

[1] Building Research Establishment, Garston, Watford , WD2 7JR, UK
[2] BG plc Property Division, Aviary Court, Wade Court, Basingstoke, RG24 8GZ, UK
[3] BG Technology, Gas Research Centre, Ashby Road, Loughborough, LE11 3QU, UK

Key words: barriers, bentonite-cement, ground water monitoring, field experiment.

INTRODUCTION

In December 1995, the Building Research Establishment in collaboration with BG plc Property Division and BG Technology began work on part of a disused gasworks site with the principal aim of assessing the in-situ performance of cement-bentonite slurry trench cut-off walls. Background information on the use and specification of cement-bentonite and HDPE barriers is given in BRE Digest 395 and ICE (1996). This type of in-ground barrier has been in use for more than 20 years in the UK to control the lateral migration of pollution from contaminated land sites and there are few known cases of unsatisfactory performance. However, there is a lack of in-situ performance data and concerns inevitably exist about their long term performance particularly in chemically aggressive ground.

Some of the initial findings from the test site and the laboratory work have been described by Tedd et al (1997). This paper outlines particular aspects of the experimental work at the site and the associated laboratory testing on the cement-bentonite. The ground conditions at the site consist of approximately 3m of made ground, containing spent oxide, coal residues, carbon black and foul lime, overlying stiff Lower Lias Clay. Consequently, there are elevated levels of sulphates and other contaminants that could potentially react with the cement-bentonite. At some locations the sulphate levels are in excess of 10 000 mg/l with a pH between 2 and 3. The water table is approximately 2m below the surface. In March 1996, two boxes 10m square in plan by 5m deep were constructed using cut-off walls to isolate parts of the site. One was constructed with a HDPE membrane and one without. Isolated lengths of wall were also constructed to assess and develop various techniques for measuring strength and permeability of the walls. Wells and piezometers have been installed to monitor water levels.

FIELD ASSESSMENT

The permeability of the cut-off walls has been measured at discrete locations by inserting devices centrally into the middle of the walls. Three approaches have been used; (a) standpipe piezometres installed when the slurry was still soft, (b) drilling into the wall and isolating a section of it using a packer system developed at BRE (Tedd et al, 1995) and (c) the piezocone. Both (a) and (b) involved carrying out falling head permeability tests. Method (a) gave permeability values of less than 1×10^{-10}m/s possibly due to blocking of the piezometer filter whereas method (b) gave values of the order of 10^{-9}m/s. Piezocone testing provided useful data about the varying strength of the different cut-off walls at the site but dissipation tests indicated permeabilities at least two orders of magnitude larger than indicated by the other in-situ measurements and

laboratory measurements, possibly due to localised cracking around the cone tip. A detailed assessment of the piezocone for this application has been reported by Tedd et al (1997). A recent excavation of a section of the wall where cone profiles had been undertaken showed the holes intact, with no obvious signs of cracking and full of water. The results imply the cement-bentonite is more deformable and less likely to crack than indicated from triaxial tests on the material.

A hydraulic gradient of approximately two has been created across the cut-off walls forming the boxes by pumping into the boxes. The amount of leakage from the boxes through or under the walls although small appears to be larger from the box without the HDPE membrane.

LONG TERM PERMEATION TESTS IN THE LABORATORY

Routine compliance testing has shown that the permeability of the set slurry was generally less than 2×10^{-10} m/s at 90 days. However, some samples from the trench that contained spent oxide had a permeability an order of magnitude higher. Permeation for longer than the 2 days required in most specifications showed a significant decrease in permeability. The interaction between the site leachate and slurry from the trench has been monitored in a permeation test at a hydraulic gradient of 20 for a year. The initial permeability of 4×10^{-9} m/s at 45 days decreased to 1×10^{-9} m/s after permeation with high sulphate, low pH site leachate and apparently remained constant for nearly a year in which time five sample volumes were permeated through the sample. Analysis of the effluent from the sample showed that both sulphate and iron were absorbed by the sample. This was later confirmed by XRF analysis of the sample. Reaction between the sample and the leachate caused a decrease in diameter and change in properties of the lower part of the sample. XRD analysis indicated that the reacted part of the sample was dominated by gypsum which was not present in the unreacted part of the sample. The results suggest deterioration of cement-bentonite cut-off walls constructed in such ground conditions, however it must be emphasised that this is an accelerated test and the ground conditions are extreme.

Future work will involve assessment of geophysical methods to detect areas of contamination, exhumation of the walls forming the boxes to detect any leakage or deterioration of the cement-bentonite and long term permeation tests in the laboratory.

REFERENCES

BRE(1994). Digest 395. Slurry trench walls to contain contamination.

ICE (1996). Draft specification for slurry trench cut-off walls construction as barriers to pollution migration. Institution of Civil Engineers, Great George St, London.

Tedd P, Quarterman R S T and Holton I R (1995). Development of an instrument to measure in-situ permeability of slurry trench cut-off walls. Proc of 4th Int. Symp. on Field Measurements in Geomechanics. Bergamo,Italy. pp 441-446.

Tedd P, Holton I R, Butcher A P, Wallace S and Daly P J (1997). Investigation of the performance of cement-bentonite cut-off walls in aggressive ground at a disused gasworks site. Proc. of the 1st Int. Containment Technology Conf. St Petersburg, Florida, USA.pp 125-132.

Tedd P, Butcher A P and Powell J J M (1997). Assessment of the piezocone to measure the in-situ properties of cement bentonite cut-off walls. Proc. of Conf. on Contaminated ground: fate of pollutants and remediation. Cardiff. Thomas Telford, pp 48-55.

RISK ASSESSMENT, MASS BALANCE AND SUCCESSFUL REMEDIATION OF A MAJOR GASOLINE SPILL IN A RESIDENTIAL AREA

Christoph Munz, René Gälli, George Kiayias and Bruno Schmid
BMG Engineering Ltd, Ifangstrasse 11, CH-8952 Zürich-Schlieren, Switzerland

Key words: risk assessment, exposure, target values, hydrocarbons, MTBE, soil vapor extraction (SVE), in-situ (bio)-remediation, groundwater modeling, natural attenuation

1. INTRODUCTION

In march 1994 a tank-car train derailed and caught fire in the suburbs of Zürich, Switzerland, losing a total of approximately 400 tons of mainly leaded gasoline. A significant amount of gasoline was able to infiltrate the subsurface. Three years later, site remediation by soil vapor extraction has been successfully completed.

2. RISK ASSESSMENT

Key issues and findings are summarized below:

Mass infiltrated: Various methods were initially used to estimate the total amount of gasoline infiltrated into the subsurface. The best estimates resulted in quantities of 50'000 to 70'000 kg, the larger number being considered more likely [1]. After completion of the remediation it is concluded that the best methods were the extrapolation from initial soil vapor extraction activities and Raoults Law. Total petroleum hydrocarbons, benzene and methyl-tert-butyl-ether (MTBE) were used as indicator parameters throughout the case study.

Vadose zone: Target clean-up values were derived by means of an exposure model as a function of future planned site uses (residential, commercial, etc). The critical exposure pathway at the site, accounting for >90% of total additional exposure, was clearly diffusion of residual gasoline vapors into the residences. The target values eventually adopted for the soil gas concentration for a future residential site use are based on a total exposure twice that of the existing background exposure. These are:

Target values in mg/m^3	benzene	total hydrocarbons
at 3 m depth	100	1'000
below 3 m depth	-	10'000

Saturated zone: A contaminant transport model was used to assess risks to groundwater for a) a short term term period resulting from the immediate and direct input of gasoline components during and after the accident, and b) for the medium and longer term period resulting from normal infiltration of rain and leaching of contaminants. Case b) proved to be negligible compared to case a). MTBE became a critical parameter as it exhibits a significant subsurface mobility and is thought to be resistant to biodegradation. Potential diffusion into residences downgradient from the site became an important aspect in defining appropriate trigger values for groundwater. In the context of a proposed intrinsic hydrocarbons bioremediation for the saturated zone the following trigger values were defined 400 m downgradient from the site: MTBE, 100 mg/L; benzene, 40 mg/L.

3. REMEDIAL MEASURES AND CONTAMINANT MASS BALANCE

Soil vapor extraction was installed at the accident site. Various optimized off-gas treatment systems were used, depending on the total hydrocarbon concentration in the extracted soil gas [2]. Extracted soil gas hydrocarbons, oxygen and CO_2 concentrations were observed on a regular basis. The cumulative mass extracted and mass degraded were calculated from these data. The overall mass balance calculated for the chosen indicator is schematically shown in figure 1. As can be appreciated, approx. an additional 60% of the mass directly extracted by SVE was biodegraded due to the venting effect.

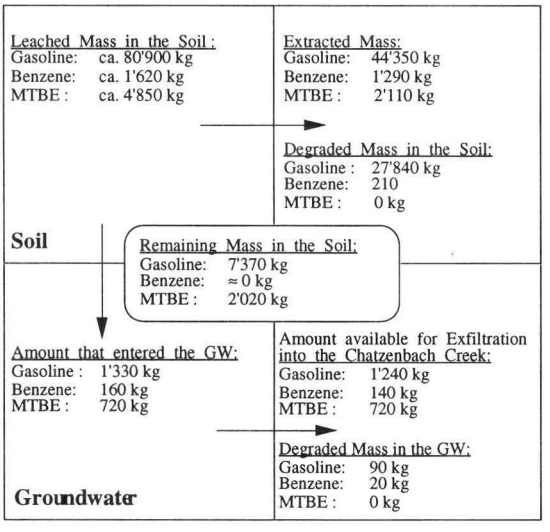


Figure 1: Mass balance for gasoline (total petroleum hydrocarbons incl. MTBE), benzene and MTBE at the end of remediation in may 1997 (38 months after the accident).

The mass balance is also a plausibility check for earlier assumptions and calculations made: a) Raoults law estimate of total gasoline infiltrated in the subsurface was short by ≈ 20%. A very good estimate considering the quantity and quality of the data available at that time; b) The large residual mass of MTBE in the soil and groundwater compartments appears rather unrealistic. Both observations could indicate a chemical and/or especially a biological degradation of MTBE [3]. Unfortunately we cannot substantiate this hypothesis, other than not being able to identify the expected concentrations in groundwater and not finding any residual MTBE in the vadose zone (soil and soil gas samples).

SVE is a very efficient and cost-effective remedial option for gasoline spills provided that off-gas treatment is optimized according to the time variant concentrations during the course of remediation. Removal costs for 1 kg of gasoline ranged from approx. Sfr 3 to 30+ from the beginning towards the end of the project, respectively.

REFERENCES

1. Munz, C., et al (1995) Derivation of risk based cleanup criteria following a major gasoline accident in a residential area, in W.J. van den Brink, R. Bosman and F. Arendt (eds.), Contaminated Soil '95 Kluwer Academic Publishers, pp. 633-634
2. Gälli, R. and LoManto, S. (1995) Remediation of a major gasoline spill caused by a train accident in Zürich, in W.J. van den Brink, R. Bosman and F. Arendt (eds.), Contaminated Soil '95 Kluwer Academic Publishers, pp. 1211-1212
3. Cooney, Catherine M. (1997) Does MTBE degrade? Environ. Sci. & Technol. 31(6), 269A

LIFE CYCLE ASSESSMENT METHOD FOR REMEDIATION OF CONTAMINATED SITES

S. Volkwein[1], A. Bender[2], W. Klöpffer[1], H.-W. Hurtig[1], G. Battermann[2], W. Kohler[3]

[1]C. A. U. GmbH, Daimlerstr. 23, 63303 Dreieich, Germany
[2]Technologieberatung Grundwasser und Umwelt GmbH, Maria Trost 3, 56070 Koblenz, Germany
[3]Landesanstalt für Umweltschutz Baden-Württemberg, Griesbachstr. 1, 76185 Karlsruhe, Germany

Key Words: Case study, databases, environmental management, environmental policy instruments, human-toxicological, life cycle assessment, life cycle impact assessment, remediation concept, software tool, toxicity

SUMMARY

In the Federal State of Baden-Württemberg, Germany, a decision tool has been developed, suitable for quantification and evaluation of environmental impacts caused by remedial action techniques. For the first time, the quantified environmental impacts of remedial actions can be taken into account in decision making, in addition to the technical or financial aspects. The basic aspects of life cycle assessment and the specific adaptations of the method to remedial action techniques are described.

KURZFASSUNG

Im Bundesland Baden-Württemberg wurde ein Instrumentarium entwickelt, das basierend auf der Methode der Ökobilanz, die Erfassung, Quantifizierung und Bewertung der Umweltauswirkungen von Sanierungsverfahren ermöglicht. Erstmals können damit neben den bisher dominierenden technischen und wirtschaftlichen Aspekten bei der Auswahl der Sanierungsverfahren auch die quantifizierten Umweltauswirkungen der einzelnen Verfahren in die Entscheidung mit einbezogen werden. Die Grundzüge der Ökobilanzierung und die spezifischen Anpassungen der Methodik für die Altlastensanierung werden im Beitrag vorgestellt.

RÉSUMÉ

Pour le pays Baden-Württemberg (Allemagne), un instrument pour l'inventaire et l'analyse et l'interprétation des impacts potentiels environnementales causés par la dépollution des sols et des eaux souterraines a été développé. La méthode est basée sur l'analyse du cycle de vie. Pour la première fois, il est possible de ne pas considérer seulement des aspects techniques et financiers dans la sélection des techniques de la réhabilitation des sites, mais aussi les impacts environnementales calculés. Les adaptations de la méthode de l'analyse du cycle de vie pour la dépollution des sols et des eaux souterraines sont expliquées. Des Premiers résultats sont montrés par un exemple.

Contaminated Soil '98, Thomas Telford, London, 1998, 1069–1070

Until now, it was not possible to quantify secondary impacts of remediation actions. The method (Volkwein et al., 1997, 1998) presented here serves for inventory analysis, classification, characterization and interpretation of secondary impacts, which are caused by the remedial action technique itself (figure 1). For the first time, this method provides a comprehensive instrument for the quantification of secondary impacts on the basis of a transparent decision making process.

The necessity of remediation is the result of a multistage procedure for the assessment of contaminated sites, including a risk assessment. The previously established necessity of the remediation is a requirement for the application of the method presented here. The method does not consider the real and potential environmental impacts induced by the cleaned-up site itself. These impacts are evaluated within the framework of the contaminated site risk assessment procedure.

The basis of the method is life cycle assessment, consisting of the phases goal and scope definition, inventory analysis, impact assessment and interpretation. For final decision making, the phase synopsis of secondary impacts and primary impacts (including the risk of the contaminated site) is added. The utilisation of life cycle assessment for the evaluation of potential environmental impacts requires specific adaptations according to the circumstances of the treatment of contaminated sites. In the inventory analysis, a set of about 60 decontamination, ensuring and secondary technologies modules have been defined.

The method was commissioned by the town of Sinsheim, developed by the C. A. U. GmbH, coordinated and technically managed by the Technologieberatung Grundwasser und Umwelt (TGU) GmbH and the Landesanstalt für Umweltschutz Baden-Württemberg (LfU), and financed by the public fund "Sonderabfallabgabe".

A software tool is under development in order to promote the inclusion of secondary impacts in the decision making process about remediation alternatives.

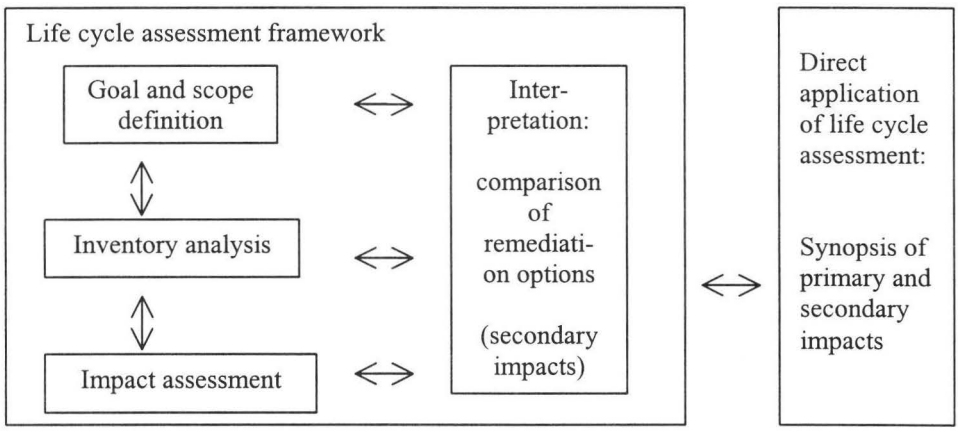


Figure 1: Remediation decision support tool based on life cycle assessment

References

Volkwein, S., Klöpffer, W. and Hurtig, H.-W. (1997): Umweltbilanz von Altlastensanierungsverfahren. Proceedings "Ökobilanzen – Trends und Perspektiven", Workshop of Gesellschaft Deutscher Chemiker (GDCh), June 26, 1997, Frankfurt/Main

Volkwein, S., Hurtig, H.-W., Klöpffer, W. (1998) Life cycle assessment of remediation of contaminated sites. Submitted to Int. J. LCA 3

Cometabolic Dechlorination of *cis*-1,2-Dichloroethene by Ethene Utilizing Bacteria

P. Koziollek, S. Bauer, D. Bryniok and H.-J. Knackmuss
Fraunhofer Institute for Interfacial Engineering and Biotechnology, Nobelstr. 12, D-70569 Stuttgart, Germany

Key words: biodegradation, bioreactors, chlorinated hydrocarbons, groundwater treatment

Introduction

Tetrachloroethene (PCE) and trichloroethene (TCE) are priority pollutants commonly present in soil and groundwater due to their widespread industrial use. Under anaerobic conditions PCE and TCE can be rapidly transformed to *cis*-1,2-dichloroethene (*c*DCE) by reductive dehalogenation (Vogel and McCarty, 1985). The anaerobic transformation of *c*DCE to vinyl chloride (VC) and ethene is significantly slower. However, under aerobic conditions, *c*DCE can be cometabolized at much faster rates.

Therefore in cooperation with the Institut für Mikrobiologie and the Institut für Siedlungswasserbau of the University of Stuttgart we are developing a process for the biodegradation of chlorinated ethenes. The process consists of two consecutive steps: an anaerobic one for the reductive dehalogenation of PCE and TCE to *c*DCE, and an aerobic one for the cometabolic turnover and mineralization of *c*DCE and, if present, VC.

The aerobic cooxidation of *c*DCE needs an auxiliary substrate that serves as energy source and an electron donor plus inducer for an appropriate monooxygenase.

Results

Currently used auxiliary substrates like methane and toluene have the serious disadvantages of low transformation yields and suicide inactivation due to the formation of highly reactive metabolites (Anderson and McCarty, 1997, Little et al., 1988, Wackett and Householder, 1989). To avoid suicide inactivation, our approach was to isolate chloroethene degrading bacteria with the use of structural analogues to chloroethenes as the enrichment substrate.

Ethene utilizing bacterial mixed cultures were enriched with ethene (3 - 20 % v/v) as the sole source of carbon and energy. Cultures were selected that were able to dechlorinate and mineralize *c*DCE completely. One mixed culture (K20) was able to degrade *c*DCE (800 µM) or VC (70 µM) and ethene (250 µM resp. 180 µM) simultaneously, both in batch and in continuous culture. The culture consisted of five bacterial strains. All were highly tolerant of *c*DCE (up to 6 mM in the liquid phase). Degradation of *c*DCE (200 µM) was not affected by the presence of TCE (100 µM) or PCE (100 µM). The specific transformation rate of *c*DCE (initial concentration 400 µM) was 8 to 9 nmol per min per mg of cell protein. The transformation yield [mol of *c*DCE/mol of ethene] was relativly high ($T_Y = 0.51$).

Continuous degradation of *c*DCE was accomplished in a stirred tank bioreactor with an operating volume of 1 liter. Release of Cl^- showed that the degradation of *c*DCE was complete when the concentration of *c*DCE in the feed did not exceed 18 µM/h.

*c*DCE degradation was optimized in a 40 liter trickling filter bioreactor with textile material (polyamide) for immobilization of the biomass. We used authentic contaminated groundwater with 2 different *c*DCE concentrations in the influx (60 µg/l or 500 µg/l, $\dot{V}$ = 5 l/h). In both cases the concentration in the efflux was below 10 µg/l. The dehalogenation rates were stable over a period of 6 months although the process was run under nonsterile conditions.

Conclusion and outlook

The advantages of ethene as an auxiliary substrate for the cooxidation of *c*DCE are: 1) high transformation yield (T_Y = 0.51), 2) simultaneous degradation of ethene and *c*DCE or VC, 3) tolerant of high *c*DCE concentrations (up to 6 mM in the liquid phase), and 4) high catabolic performance during continuous cultivation under non sterile conditions. The process described here together with the system described for anaerobic dechlorination of PCE and TCE (Wohlfarth and Diekert, 1997) can constitute a multicomponent process for clean up of groundwater and soils which are contaminated with mixtures of chloroethenes.

For this purpose authentic PCE contaminated groundwater will be used. PCE and TCE will first be dehalogenated by *Dehalospirillum multivorans* in 30 liter fixed bed reactor (anaerobic step) followed by cometabolism of the *c*DCE in a 40 liter trickling filter bioreactor (aerobic step).

References

Anderson J. E., and P. L. McCarty. 1997. Transformation yields of chlorinated ethenes by a methanotrophic mixed culture expressing particulate methane monooxygenase. *App. Environ. Microbiol.*, 63:687-693.

Little, C. D., A. V. Palumbo, S. E. Herbes, M. E. Lidstrom, R. T. Tyndall, and P. J. Gilmer. 1988. Trichloroethylene biodegradation by a methane-oxidizing bacterium. *Appl. Environ. Microbiol.*, 54:951-956.

Vogel, T. M., and P. L. McCarty. 1985. Biotransformation of tetrachloroethene to trichloroethene, dichloroethene, vinyl chloride, and carbon dioxide under methanogenic conditions. *Appl. Environ. Microbiol.*, 49:1080-1083.

Wackett, L. P., and S. R. Householder. 1989. Toxicity of trichloroethene to *Pseudomonas putida* F1 is mediated by toluene dioxygenase. *Appl. Environ. Microbiol.*, 55:2723-2725.

Wohlfarth, G., and G. Diekert. 1997. Anaerobic dehalogenases. *Curr. Opin. Biotechnol.*, 8:290-295.

Acknowledgement

The project was supported by the Deutsche Bundesstiftung Umwelt, Osnabrück.

GROUNDWATER TREATMENT PLANT AT THE FORMER GASWORK REMEDIATION SITE "GRIFTPARK" IN UTRECHT, THE NETHERLANDS. THE SELECTION OF A DEFINITE WATER TREATMENT SYSTEM

M.P. Pluim[1)], P.W. de Vries[1)], F.I.H.M. Oesterholt[2)] and J.J.M. Appelman[3)]

[1)] Municipality of Utrecht, Project office Griftpark, P.O.Box 8406, 3503 RK Utrecht, The Netherlands
[2)] NUON Water, Postbus 8002, 6880 CA Velp (before TAUW), The Netherlands
[3)] TAUW Environmental Consultancies and Labotories, P.O. Box 133, 7400 AC Deventer, The Netherlands

KEYWORDS

Gaswork; groundwater treatment; pilot plant; biological treatment; physico-chemical processing; UV-oxidation; ozone; PAH; mineral oil; cyanide;

INTRODUCTION

The Griftpark site is one of the most well-known and largest remediation sites in the Netherlands. The location, situated just outside the centre of Utrecht, measures about 10 hectares. The severe soil pollution was caused by the presence of three gas manufacturing plants and some other activities (1850 - 1959). The highly contaminated source area (BTEX, PAH, cyanide, phenols and mineral oil) has been isolated by grondwater permanent withdrawal in combination with a bentonite screen wall (length 1250m, depth 60m). Besides this, grondwater remediation is needed outside the screen wall during a period of 100 years before discharging into the lokal sewerage (see tabel 1).

parameter	unit	influent concentration	effluent demand
cyanide (tot)	µg/l	50	150
COD	mg/l	125	-
BOD	mg/l	40	-
phenols	µg/l	140	100
BTEX	µg/l	5.500	15
naphtalene	µg/l	3.800	15
PAH light fr. heavy fr.	µg/l	 500 820	5
mineral oil	µg/l	13.400	100

Table 1. Overview of the average groundwater quality Griftpark and the effluent demand

PILOT PLANT SYSTEM

In view of the length of the grondwater withdrawal, the expected high volume rates (200 m3/h) and the high treatment costs, the Province of Utrecht has decided to build a semi-permanent full-scale pilot plant consisting of several potential water treatment technices. This pilot plant system consists of 4 parallel treatment lines:

- 2 lines (each 12.5 m^3) with proved physical/chemical treatment technices;
- 2 lines (each 12.5 m^3) with "new" biological treatment technices.

In addition, an ozon/UV-unit (capacity 12.5 m3/h) can be tested on the effluent of each treatment line or be used as pre-treatment of the biological lines.
The pilot plant is intensively tested (oktober 1995 - oktober 1996) to find the economically and technologically most optimal configuration of treatment technices for the specific Griftpark-conditions.

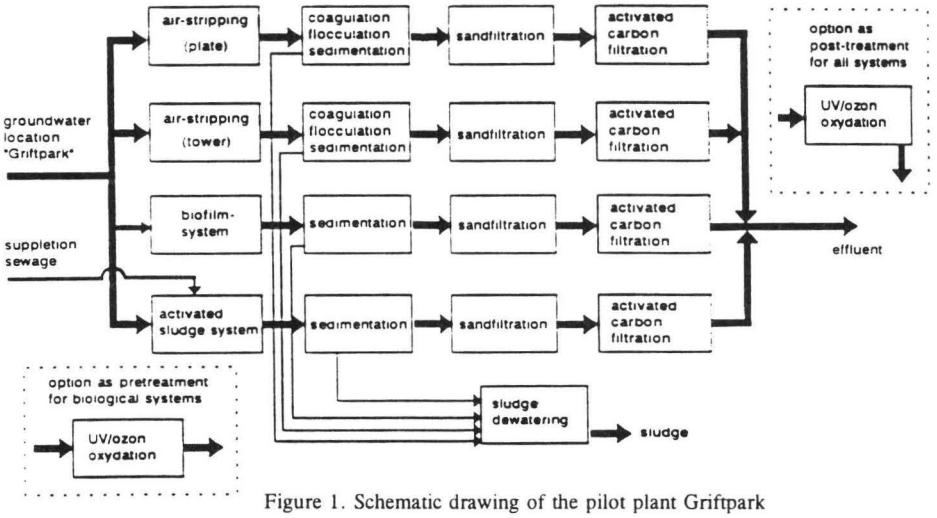


Figure 1. Schematic drawing of the pilot plant Griftpark

RESULTS AND CONCLUSIONS

Although the coagulation/flocculation/sedimentation-process is a proven treatment technic for the present components it was not possible to reach stable conditions during the testing period. The system was not flexible to operate under various influent qualities. An economic evaluation of this process has resulted in the decision to stop further research.
Research on the "new" biological systems has resulted in a close finish, economically as well as technologically. Both biological systems has shown a removal efficiency of 90%-95% for all components, except the heavy fraction PAH (60%-85%) and cyanide (0%). Besides the filtration of suspended solids a considerable biological activity of the sandfiltration was found. Treatment costs for both biological systems are calculated to be approximately *f* 0.35 /m3 (excluding costs for a building construction), while these costs were estimated to be *f* 3.50/m3 before starting the research.
Because of the proven flexibility, the small sludge production and the absence of mechanical parts the activated sludge system is chosen as the groundwater treatment system for the definite treatment plant Griftpark.

Treatment of contaminated soil and dredged harbour sludge by a new flotation approach.

H.A.E. Mulleneers[†], H. Bruning[†], L.K. Koopal[‡], W.H. Rulkens[†]

[†] *Wageningen Agricultural University, sub-department of Environmental Technology, Bomenweg 2, 6703 HD, The Netherlands.*
[‡] *Wageningen Agricultural University, Laboratory for Physical Chemistry and Colloid Science, Dreijenplein 6, 6703 HB, The Netherlands.*

Keywords: Flotation, PAH, contaminated soil, reactor, clean-up technologies, fine particles, classification, off-site treatment, sediments.

Introduction

In the Netherlands, millions of tons of harbour sludge and river sediment have to be dredged. Part of this sludge and sediment is contaminated and has to be cleaned. Next to this thousands of contaminated sites require clean-up. Mostly the remediation finds place off-site, by physical/chemical classification using hydrocyclones. The process is based on separation of clean and contaminated particles by their differences in size and density. This kind of treatment has proven to be very successful, especially for the course fraction of the sludge/soil. For the fines fraction (20 - 90 μm) the process is often less successful. Flotation techniques which are, next to density and size, also based on surface characteristics, could be an alternatives to remediate this fraction.

In the soil remediation flotation process, contaminated particles should selectively attach to airbubbles and float to the surface. This will result in a highly contaminated floating froth and a clean tailing. The flotation technique is far from new and has been used in applied mineralogy for almost 100 years [1]. The mining industries focus on a high amount of valuable minerals in the concentrate whereas the environmental flotation aspects are basically focused on a clean tailing. Most industrial particle separation techniques make use of bulk properties and therefore don't work on a micro level. This makes that flotation equipment for the refinement of ores, as used in the mining processes, cannot be used for the small soil particles (< 63/90 μm). The high turbulence and large bubbles in those reactors will cause an entrainment and entrapment of the small particles. Therefore modifications are needed in both the area of reactor design as in the use of surfactants, to make flotation a successful technique in the remediation of contaminated soil.

The flotation of fine particles implicate that also small bubbles should be generated. Large bubbles don't have enough affinity with the small particles and can also easily entrap them. Dissolved air flotation (air bubbles are generated from water which is saturated with air at high pressure) appeared to be a satisfying method to create the small bubbles. Another step in the process is the separation of froth and clean particles. Sedimentation rates of the small particles are very low. In a apparatus which is well adjusted to achieve a good contact between bubbles and particles the sedimentation of the clean particles would become a problem. Entrainment of these particles will bring

them into the froth which will lower the grade of the flotation process. This forced us to develop a special apparatus in which the flotation process is combined with a lamella separator on top of the mixing zone [2]. An improved apparatus is in progress which will enhance the sedimentation by counter current laminar streams. This will also allow us to float even smaller particles below 20 μm.

Results

We have determined the flotation aspects of a classificated sludge and dredged Overschie- and (Amsterdam) Petroleum harbour sludge. The classificated sludge came from a Dutch soil cleaning company (BSN). It contained particles, silica and soot (coal), between 20 and 90 μm. The soot particles are a result of uncompleted combustion and are ended up in the soil by deposition. Their presence cause a contamination with polynucleic aromatic hydrocarbons (PAHs). Charge measurements of the particles indicated that on both the silica and the soot surface carboxylic and hydroxylic groups are present. The hydroxylic groups on silica are partly phenolic, similarly as those on the soot surface. The PAH contamination in the Overschie- and Petroleum harbour sludge was also caused by coal like particles.
Flotation experiments on labscale are presented in table 1. Experiments were carried out with fuel oil or Aerophine as collector.

Table 1:

sludge	particle size (μm)	initial PAHs (mg/kg dm)	tailing PAHs (mg/kg dm)	dry matter (%) tailing
BSN-soil	20-90	26	2	98
Overschie-harbour	45-90	32	3	93
Overschie-harbour	125-200	44	1	97
Petroleum-harbour	45-90	421	44	61
Petroleum-harbour	125-200	200	5	91

The results show that flotation is an adequate method to remove PAH-containing particles from the tested sludges. The flotation process was highly selective. Except for the Petroleum harbour sludge (45-90) the clean silica-particles were hardly entrapt or entraint into the froth and only the contaminated coal particles were floated. The Petroleum harbour sludge (45-90) showed a relatively low dry matter content in the tailing (61%). This is most probably caused by agglomeration of silica and coal-like particles due to the high initial oil concentration.

1. Ives, K.J. (1984) *Scientific basis of flotation.*, The Hague, Martinus Nijhoff.
2. Bruning, H., (1995) Flotation in contaminated soil treatment, in W.J. van den Brink, R. Bosman, F. Arendt (Eds.) Contaminated soil '95, Kluwer Academic Publishers, Dordrecht, Vol II, pp. 1169-1170.

SOIL AND GROUNDWATER RESEARCH OF THE AMERICAN PETROLEUM INSTITUTE

Bruce J. Bauman, Soil & Groundwater Research Program Coordinator
American Petroleum Institute, 1220 L Street NW, Washington, D.C. 20005

Key Words: programme of research, petrol hydrocarbons

The American Petroleum Institute (API) is the trade association for the petroleum industry in the United States, and is the source of several hundred technical standards for the operating segments that comprise the industry: exploration and production, refining, transportation and marketing. API also engages in research activities to support those industry operations provide continuous improvement in operational and management practices. In addition to its extensive activities evaluating air quality, surface water and health effects of petroleum hydrocarbons, it has had an active soil and groundwater research program for over two decades, addressing the environmental behavior and remediation of refined products, crude oils and hydrocarbon wastes. This work is primarily carried out under the guidance of the Soil/Groundwater Technical Task Force.

The current structure and research focus of this group reflects the key processes involved in dealing with contaminated properties: site characterization and remediation; biodegradation and natural attenuation processes; risk assessment and site closure. The fate, transport and remediation of gasoline oxygenates, especially MTBE, is also a primary focus of the group. The prime objectives of this program are to provide:

- technical support for implementation of risk based corrective action policies;
- input to regulatory decision making processes during establishment of cleanup standards and waste management policies;
- improved remediation practices and technologies;
- education and training to API members, regulators, consultants, and others.

With the broad acceptance of risk based approaches to corrective action there has been an increased need for techniques and tools to evaluate exposure pathways, including potential ecological impacts. Such evaluations require the accurate estimation of the fate and transport of dissolved and vapor phase hydrocarbons in the vadose and saturated zones. Current projects are developing improved approaches to evaluating the flux of leachate (Rixey, 1996) and vapor from residual sources in soils. Modeling tools are also being developed to facilitate site specific application of this improved understanding of hydrocarbon transport. A screening level approach to rapidly assessing the dilution / attenuation of BTEX in the subsurface has recently been completed (API, 1998)

Intrinsic biodegradation processes have been a key topic of research for over a decade, and both laboratory and field projects are in progress to provide better characterization of the mass transformation rates and the biogeochemical factors that influence them both in soil and groundwater. Two recent studies have been published that provide guidance on the use of sampling and analytical techniques for characterizing intrinsic biodegradation (API, 1997a&b). A comprehensive literature review of lab and field studies of anaerobic biodegradation for 33 chemicals was used to generate a database of first order

Contaminated Soil '98, Thomas Telford, London, 1998, 1077–1078

biodegradation rate constants, and was recently submitted to the U.S. EPA to facilitate their assessment of contaminant fate and transport (Aronson and Howard, 1997). Recent increased regulatory interest in MTBE and other oxygenates has led to an accelerated effort to characterize their fate and transport in soil and groundwater. API research activity on MTBE is summarized in another paper at this conference (Bauman, 1998)

A screening methodology for evaluating ecological risks is in the final stages of completion, and an updated version of API's Decision Support System software for contaminated site risk assessment (Claff, 1997) is being beta tested before final release. Other final reports in progress and expected to available in 1998 include:
a field evaluation of the performance and effectiveness of air sparging; an evaluation of the necessity of hydrocarbon removal from source zones in relation to risk reduction (Beckett and Lundegard, 1997), and a comparison of two free product recovery methods.

In conjunction with the National Ground Water Association, the Task Force conducts an annual conference to serve as a forum for discussion of new findings (NGWA, 1997). As a means to effectively communicate the results of its research to a diverse, international audience, the Task Force is increasing its use of electronic media and the Internet. Information on current API research publications and a variety of other useful resources can be accessed through the API website at **http://www.api.org**.

API. 1997a. Effects of Sampling and Analytical Procedures on the Measurement of Geochemical Indicators of Intrinsic Bioremediation: Laboratory and Field Studies. API Publ. 4657. API, Washington D.C.

API. 1997b. Methods for Measuring Indicators of Intrinsic Bioremediation: Guidance Manual. Publ. 4658. API, Washington D.C.

API. 1997c. Field Studies of BTEX and MTBE Intrinsic Bioremediation. Publ. #4654. American Petroleum Institute, Washington, D.C.

API. 1997d. Delineation and Characterization of the Borden MTBE Plume: An Assessment of MTBE Transport in Groundwater Over 8 Years. Publ. 4668 American Petroleum Institute, Washington, D.C.

Aronson, D. and P.H. Howard. 1997. Anaerobic Biodegradation of Organic Chemicals in Groundwater: A Summary of Field and Laboratory Studies. A report prepared for API, CMA, NCASI, EEI and AFPA. API, Washington, D.C.

Bauman, B.J. 1998. Subsurface Fate and Transport of Oxygenates. (This Proceedings)

Beckett, G.D. and P. Lundegard. 1997. Practically Impractical - The Limits of LNAPL Recovery and Relationship to Risk.

Claff, R.C. 1997. The API Decision Support System for Risk and Exposure Assessment. p. 347-372 in "SESOIL in Environmental Fate and Risk Modeling". Bonazountas, M. et al. eds. Amherst Sci. Publ. Amherst MA.

Garg, S. and W.G. Rixey. 1997. The Dissolution of BTX and Naphthalene from an Insoluble, Residually Trapped NAPL in a Non-Sorbing Porous Medium. Submitted to J. of Contam. Hydro.

National Ground Water Association. 1997. Conference proceedings: Petroleum Hydrocarbons & Organic Chem. in Ground Water. 801 pp. NGWA, Westerville, OH.

Rixey, W.G., 1996. The Long-Term Dissolution Characteristics of a Residually Trapped BTX Mixture in Soil. Haz. Waste and Haz. Mat.: 13(2) pp. 197-211.

A CASE STUDY OF THE REMEDIATION OF SOIL CONTAMINATED WITH POLYCHLORINATED BIPHENYLS (PCBs) USING LOW TEMPERATURE THERMAL DESORPTION

NORRIS, G.[3] AL-DHAHAIR, Z.[2] and BIRNSTINGL, J.G.A.[1]
[1] *Nortel plc, Oakleigh Road South, New Southgate, London, N11 1HB, UK*
[2] *Golder Associates (UK) Ltd. 54-70 Moorbridge Rd. Maidenhead, Berks, SL6 8BN, UK*
[3] *British Aerospace Royal Ordnance Environmental Services Group, Westcott, Aylesbury, Buckinghamshire, HP18 ONP, UK*

Key words: Thermal treatment, PCB (polychlorinated biphenyls), chlorinated hydrocarbons, clean-up operation, remediation.

INTRODUCTION

The PCB contaminated soil discussed in the present study arose from a 20ha telecommunications manufacturing facility built in the 1950s. Capacitor manufacture, and retrofilling of capacitors and transformers led to contamination of the soil in a number of small areas on the site. It is believed that subsequent cut and fill construction operations spread the contamination over large areas of the site. Under contract from *Nortel Ltd, Golder Associates (UK) Ltd.* resolved the contamination problem. Potential remedial alternatives investigated included the use of landfill, soils washing, solvent washing, bioremediation, high temperature incineration and low temperature thermal desorption. Following technology evaluation studies, including a number of treatment trials, low temperature thermal desorption was selected for the treatment of the most highly contaminated material. Treatment was undertaken by *British Aerospace Royal Ordnance Environmental Services Group* (ESG) using a 20 t/h mobile unit.

DISPOSAL ROUTES FOR THE CONTAMINATED SOIL

The average PCB concentration measured in the ground was 120mg/kg, with a peak of 1300mg/kg. These concentrations are well outside the permissible limits in landfills, which currently stand at 20mg/kg, therefore disposal to a licensed landfill was not an option. High temperature incineration was a viable alternative, however, the high costs of around £770 per tonne, including drumming the waste and hauling it to a licensed incinerator, were prohibitive since the total cost would have been around £1.8m for the treatment of the 1200m^3 of soil. More cost effective solutions were therefore explored.

The soil washing option using water to separate the clean coarser particles from the contaminated finer fraction of the soil was studied and discounted, since the small volume of soil did not make this commercially viable. Furthermore, the process would have resulted in around 40% of the fine fraction of the soil requiring further treatment. The next option considered was bioremediation. Two specialist companies were engaged independently to carry out laboratory scale experiments on samples obtained from the site. The tests allowed for two steps; the reduction of the chlorine content of the PCBs using chemical reagents, and the degradation of the low chlorine PCB congeners by special strains of bacteria imported from either the USA or Germany. Whilst some progress was made with the second step on non-site low chlorine PCB

congeners, it was found that the chemical by-products produced in the first step on the site PCBs were toxic to the bacteria. Both companies independently decided to abandon the bioremediation route and to recommend the solvent washing technique instead. The solvent washing technique has been used in the USA since 1994 and a considerable body of experience exists. In the UK, the technique is in its development and field trial stages only. A local company with patented slurry mixer was engaged to carry out a selection of appropriate solvent and laboratory scale trials. Some progress was made on the solvent selection, but it soon became apparent that the time required to complete the trials and the relatively high associated development costs made this option unattractive.

LOW TEMPERATURE THERMAL DESORPTION

Low temperature thermal desorption at around 400 °C is a proven remediation technology suitable for the treatment of soils contaminated with low and middle distillate organic compounds such as solvents, gasoline, diesel and lubricating oils, and some pesticides. Contaminated material is continuously fed through a rotary kiln where it is heated to temperatures sufficient to evaporate/combust the contaminants, effectively stripping them from the soil. The exhaust gases and any non-combusted vapours then pass through dust filters into a thermal oxidiser unit or afterburner, where controlled oxidation at a minimum temperature of 850 °C ensures extremely high destruction efficiencies of the contaminant vapours. Following successful treatment trials, the technology was used to treat the contaminated soil from the site in question.

RESULTS

	CO	SO_2	NO_x	VOC[1]	HCl	HF	Dioxins[2]
Value	9.4	< 5	165	15	5	1.5	0.01
Consent	100	50	190	20	10	2	1

All data except for dioxins are expressed in mg/m^3 corrected to 11% O_2, dry at STP
[1] Total Organic Carbon
[2] Toxicity equivalent (TEQ) ng/m^3 corrected to 11%, dry at STP.

	Total Particulate	Total metals	PCB[1] (Output Soil)
Value	14.5	0.15	0.1 ± 0.1
Consent/Target	20	1	1

All data are expressed in mg/m^2 corrected to 11% O_2, dry at STP.
[1] Sum of congeners 28, 52, 101, 118, 138, 153 and 180.

CONCLUSIONS

The above results demonstrate effective remediation of PCB contaminated soil using low temperature thermal desorption. Thermal treatment has been shown to remove PCBs from a difficult soil matrix sufficiently for the soil to pass stringent residual contamination values, without unacceptable impacts on the environment and at a cost per tonne significant lower than that of high temperature incineration - the remediation using low temperature thermal desorption presented a saving of 75%.

BBT-SECTOR SURVEY SOIL REMEDIATION TECHNIQUES

Gevaerts W.[1], Pijls C.[2], Dijkmans R.[3], Dries V.[4]
[1] Tauw Milieu nv, Leuvensesteenweg 542, 1930 Zaventem, B
[2] Tauw Milieu bv, P.O. Box 133, 7400 AL, Deventer, NL
[3] VITO, Boeretang 200, Mol, B
[4] OVAM, Kan. De Deckerstraat 22-26, 2800 Mechelen, B

Keywords: classification, clean-up technologies, data bases, decontamination techniques, environmental policy instruments, knowledge transfer, priority lists, ranking system, remediation concept, soil remediation.

Introduction

On the request of the Flemish Government, the Flemish Institution for Technological Research[1] has established an Information Centre on Best Available Technologies (BBT)[2]. The soil remediation sector is one of the subjects on which a BBT-study is carried out.

The study consists of two parts:
- drawing up an inventory of the various soil remediation techniques which, depending on the situation, may be considered as BBT;
- developing a system to facilitate decision-making in the process of selecting these techniques (Decision Support System: DSS).

The results of the study intend to serve the Public Waste Agency of Flanders[3], the authority in charge of soil remediation, as an internal tool in assessing remediation plans. The system is also intended to help other users (environmental managers and soil remediation professionals in Belgium and abroad) select the technique best suited to deal with their specific contamination problem.

The characteristic features of the project are:
- the innovative character of the decision support system (the resulting system is the first ever worked out in Europe);
- the data base and the DSS will be made available on the Internet;
- the DSS will be constructed as an easy assessable and useful tool for both laymen and professionals.

Inventarisation

The inventory contains all techniques of which pilot-scale testing was completed with proven success. This applies to both conventional techniques (such as the excavation of contaminated soil), and techniques developed only recently (such as the use of electroreclamation in remediating hydrocarbon contaminations). A

---

1 Vlaamse Instelling voor Technologisch Onderzoek (VITO)

2 Best Available Techniques (BAT) stands for those techniques (i.e. technologies and organisational measures) available on the market which, produce the best environmental results at a reasonable cost price.

3 Openbare Afvalstoffenmaatschappij van het Vlaamse Gewest (OVAM)

technical data sheet is produced for each individual technique, containing a short description of the technique as well as information on applicability conditions, remediation efficiency, cost price, security issues and environmental yield. The environmental yield is determined qualitatively by comparing the technique in question with other possible methods in terms of energy consumption, residue production, spatial requirements and nuissances due to odour and noise emissions. The data sheet on newly developed techniques also includes a reference list.

Decision support system

The DSS is meant as a tool to perform an initial technical screening of remediation options, possibly fit to tackle the contamination problem.

The present contamination situation is fed into the input module, which is partly organised in a graphic way (e.g. the soil structure) and partly in a textual way. The most important input data refer to: the soil structure, contaminants, general factors to be taken into account such as buildings and structures present, risk of damages due to subsidence, remediation targets and duration of the clean-up operation.

The output of the decision support system distinguishes three different levels:
1. The remediation method: a method is an all including name, comprised of a sequence of concepts suitable to remediate a contamination (e.g.: *excavation* is the remediation method applied).
2. The remediation concept: a concept is a collection of similar remediation techniques. The connection between the various techniques making part of a concept is the general principle of the technique (i.e. which is its purpose), (e.g. the various successive concepts in *excavation* are: lowering the groundwater table; excavating the soil material in the dry; transporting the material; treating the soil).
3.The remediation technique: (e.g.: the selected techniques for *excavation* are: vacuum drainage; excavation; road transportation; physico-chemical soil treatment).

This results in a general summary of methods, reviewing the applicable, irrelevant and, from a technical point of view, impossible methods. The system also determines which data are crucial for a sound assessment of its applicability.
The methods are ranked considering risk reduction, contaminant reduction, environmental yield and costs.

The data base is built in MS-Access, the decision-making support system in Visual Basic. The technical data sheets and the decision-making support system is made available on Internet as part of the Flemish EMIS-data bank. The structure of the system is set-up in such a manner that new techniques can easily be added to the data base and the decision support system.

CONTROLLED AND TARGETED MOBILISATION OF COPPER IN SOIL TO ENHANCE ITS ACCESSIBILITY FOR "REMEDIATION-PLANTS"

K. Wenger[1] and S. K. Gupta[1]

[1]Swiss Federal Research Station for Agroecology and Agriculture FAL, Institute for Environmental Protection and Agriculture IUL, Schwarzenburgstrasse 155, CH-3003 Bern, Switzerland

Keywords: Contaminated soil, in-situ bioremediation, heavy metals, bioavailability, mobility, copper

SUMMARY

Our research group is presently investigating methods to enhance metal uptake by high biomass plants with a controlled and targeted mobilisation. The objective is a significant reduction of the remediation time.

Pot experiments with a calcareous soil were carried out and the effect of the application of mobilising agents such as NTA (and citric acid, on copper uptake by tobacco and maize was studied. It was found that NTA increased the copper uptake by maize roots, whereas no effect was observed on tobacco roots.

Introduction

The largest part of heavy metals in arable soils is either adsorbed on soil particles or bound to organic matter, and is not available for plants. Bound heavy metals can be made available by decreasing soil pH (Gupta 1992, Herms and Brümmer 1980) or by an increase of soluble organic complexing agents. Wallace et al. (1974) described the mobilisation by synthetic chelates, e.g. EDTA (Ethylenedinitrilotetraacetic acid) and NTA (Nitrilotriacetic acid). The addition of chelates to a Pb-contaminated soil greatly increased Pb concentrations in shoots of corn (Zea mays L. Cv. *Fiesta*) and pea (Pisum sativum L. Cv. *Sparkle*) (Huang et al. 1997). Any increase in bioavailable heavy metals in soil poses a risk of metal leaching to deeper soil layers or to groundwater. Therefore, a controlled increase of the plant available heavy metal fraction in soil should be attempted. The process should be controlled in order to avoid loss of heavy metals by leaching, to provide a maximum of soluble heavy metals available for removal and to maintain a constant available metal flux in soil solution throughout the maximum growth period of plants. By using plants to extract metals from soil, the optimal concentration of soluble heavy metals must be adapted to the uptake capacity of the particular plant. In order to prevent an undesirable accumulation of mobilising additives it is preferable to use substances that are degradable by microorganisms. Depending on the substance used for mobilisation it might be necessary to repeat the mobilisation treatment several times at a low dosage throughout the decontamination process, e.g. during the vegetative period. The intervals between each treatment will be determined by the rate of degradation process of the substance in soil.

Methods and materials

The soil sample used for pot experiments was collected from the topsoil (0 to 20 cm) of a calcareous soil, near a metal smelter, in a zone of high contamination with copper, zinc and – to a lesser extent – cadmium. The soil had an average pH of 7.6 and a C_{org} content of 5.3%. Total heavy metal concentrations, determined by nitric acid extraction according to the Swiss ordinance relating to pollutants in soil (VSBo 1986), amounted to 695 mg/kg dry soil for zinc, 524 mg/kg for copper, and 2.7 mg/kg for cadmium.

Each pot was filled with 9 kg of soil. After filling in 3 kg, and 6 kg of soil a perforated PVC ring with a connecting piece to the surface was put into the pot. Maize (Zea Mays

LG 11) was sown and tobacco (Nicotiana tabacum *Bad. Geudertheimer*) was planted and the plants were grown in a greenhouse. Different doses of mobilising agents such as 1 mmol NTA (NTA 1), 2 mmol NTA (NTA 2), 50 mmol Citric acid (C.A. 1), or 100 mmol Citric acid (C.A. 2) were added to each pot. Citric acid was added twice a month dissolved in 30 ml NANOpure water, NTA was added once a month dissolved in 20 ml NANOpure water. Each treatment was repeated three times. After 25, 52 and 91 days the tobacco and maize plants were harvested.

Results and discussion

The effect of the various additions of mobilising agents on the copper uptake by tobacco and maize roots at different growth stages is shown in figure 1. The highest copper concentration was found in maize roots after treatment with NTA. NTA increased the copper uptake by maize through mobilisation by a maximal factor of approximately 2. Hasselbach and Boguslawski (1991) found an increase in heavy metal uptake by plants by a factor 2 to 3 by decreasing soil pH about 1 unit. After 25 days of treatment with NTA 1 the copper concentration in maize roots was about 400 mg/kg dry matter. After 52 days and 91 days of NTA treatments, a decrease in copper uptake was observed. This could be evidence of a dilution effect, caused by root growth. In compare to maize, tobacco showed a considerable decrease in yield (results not shown). The physiological growth of tobacco might have been affected due to copper concentration in soil.

A main task for the future is to find a better system to distribute the mobilising substance more homogeneously in the vicinity of the plant roots. Further studies are needed to find suitable application doses and application frequency of mobilising agents.

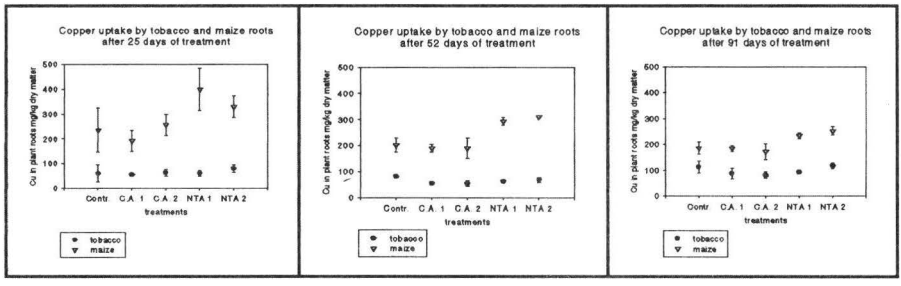


Figure 1: Effects of mobilising agent application on copper uptake by tobacco and maize roots

References

Gupta, S.K. (1992) Mobilizable metal in anthropogenic contaminated soils and its ecological significance, In: J.P. Vernet (ed.) Impact of Heavy Metals on the Environment, Elsevier, Amsterdam.

Hasselbach, G. and von Boguslawski, E. (1991) Bodenspezifische Einflüsse auf die Schwermetallaufnahme der Pflanzen, In: D. Sauerbeck and S. Lübben (eds.) Auswirkungen von Siedlungsabfällen auf Böden, Bodenorganismen und Pflanzen, Berichte aus der ökologischen Forschung, Band 6.

Herms, U. and Brümmer, G. (1980) Einfluss der Bodenreaktion auf Löslichkeit und tolerierbare Gesamtgehalte an Nickel, Kupfer, Zink, Cadmium und Blei in Böden und kompostierten Siedlungsabfällen, *Landwirtschaftliche Forschung, 33,* pp. 408-423.

Huang, J.W.W., Chen, J.J., Berti, W.R., Cunningham, S.D. (1997) Phytoremediation of lead-contaminated soils: Role of synthetic chelates in lead phytoextraction, *Environmental Science & Technology 31,* 3, pp. 800-805.

VSBo (1986) Swiss Ordinance Relating to Pollutants in Soil. Verordnung des Schweiz. Bundesrates, Eidg. Drucksachen- und Materialzentrale, Bern, Switzerland, SR 814.12.

Wallace, A., Mueller, R.T., and Alexander, G. (1974) Effects of high levels of NTA on metal uptake of plants grown in soils, *Agron. J.*, 66, pp. 707-708.

ENHANCED VERTICAL BARRIERS FOR COMBINED ISOLATION AND TREATMENT

Jeffrey C. Evans[1] and Michael J. Prince[2]

[1]Professor of Civil Engineering, Bucknell University, Lewisburg, PA 17837 USA
[2]Associate Prof. of Chemical Eng., Bucknell University, Lewisburg, PA 17837 USA

Keywords: slurry wall, adsorption, computer simulations, clay, barriers, partitioning

INTRODUCTION

Vertical barriers have long been used as key components in waste isolation systems. In the US, vertical barriers for waste isolation are almost always installed using the two-stage method resulting in a soil-bentonite cutoff wall and designed based predominantly upon considerations of hydraulic conductivity. The paper describes the enhancement of conventional soil-bentonite cutoff walls to improve their capacity as active treatment zones while maintaining their desirable characteristic of low hydraulic conductivity. Specifically, this paper describes the investigation of a soil-bentonite barrier material from a contaminated site in the US which was enhanced with attapulgite and calcium chabazite to improve the barrier capacity to attenuate the transport of a selected inorganic contaminant (cadmium), and the application of these data in contaminant transport modeling to demonstrate the improvements in expected field performance of enhanced barriers as compared with the traditional barrier. These studies provide further support to the concept that low permeability contaminant transport barrier performance can be enhanced through the addition of mineral additives (Evans, Adams, and Prince, 1997, Evans, et. al., 1997).

METHODOLOGY

The improvement in treatment capability was assessed using batch extraction tests. From these tests, adsorption isotherms were developed which, in turn, were analyzed over the linear region to yield the equilibrium distribution coefficient, K_d. This value is taken to represent the partitioning of ions between the liquid and solid phase. Equilibrium is quantified by the amount of solute adsorbed per mass of adsorbent versus the concentration of solute in solution at equilibrium. These data were used in a modeling comparison using the advection-dispersion-adsorption equation solved for the specific boundary conditions normally associated with a vertical barrier. Previous studies demonstrated this approach where column studies were conducted and the results from the long-term column tests were in good agreement with those predicted using the coupled isotherm-modeling approach (Evans and Prince, 1997).

LABORATORY RESULTS

The K_d value for the as-mixed soil from the slurry wall construction site was first determined and the impact of liquid to soil ratios evaluated. Using liquid to soil ratios varying from 800:1 to 100:1, the average K_d value was found to be 58 (r^2=0.97), 64 (r^2=0.99), 58 (r^2=0.97), 66 (r^2=0.997), and 72 (r^2=0.999). These data demonstrate a slight dependence upon soil-water ratio. Two enhanced backfill mixtures were prepared by adding 2% by dry weight mineral enhancement. One mixture used attapulgite while the other used calcium chabazite and the K_d values were determined at a liquid to soil ratio of 400:1 to be 127 (r^2=0.92) and 236 (r^2=0.82), respectively.

Contaminated Soil '98, Thomas Telford, London, 1998, 1087–1088

MATHEMATICAL MODELING OF ENHANCED BARRIERS

These laboratory data, along with typical field conditions, were used to compare the projected breakthough time for each of the three backfill mixtures. Contaminant transport was modeled using the widely published advection-dispersion-adsorption equation. To simulate field conditions; assumptions included a wall thickness of 75 cm, a hydraulic gradient of 1.0 and a porosity of 0.4. The interstitial velocity was calculated from Darcy's law. The bed density was calculated from phase relationships assuming a density of solids of 2.65 g/cm^3.

The dispersivity was calculated from an empirical correlation (Rowe et al., 1995) where the average grain size was assumed to be 50 microns (grain size) and the molecular diffusivity to be 5e-6 cm^2/sec.. This information, coupled with experimentally derived partition coefficients and the advection/dispersion equation was used to predict contaminant break-through times (defined to be Ce*= 0.05) for each barrier material. The hydraulic conductivity was modeled as 1x10^{-10} m/s, as measured in laboratory hydraulic conductivity tests on these materials.

RESULTS

Break-through curves for the base soil and the enhanced backfill mixtures were generated from the modeling effort described above. The time for breakthrough for cadmium through the unenhanced material was 117 years. The breakthrough time was improved to 236 years and 473 years for attapulgite and calcium chabazite enhanced materials, respectively.

CONCLUSION

This study has presented evidence for improved design of soil-bentonite slurry trench cutoff walls for containment of contaminants in the subsurface. Conventional soil-bentonite vertical barriers are designed and built as hydraulic barriers. These studies show that these hydraulic barriers can be enhanced to significantly retard the transport of metals such as cadmium.

ACKNOWLEDGEMENTS

The authors would like to thank Steve Day of GeoCon/WCC, and James Cherewatti, Ashin Parikh, Mike McLane and Dr. Elaine Keithan, of Bucknell University for their contributions to this effort.

REFERENCES

Evans, J. C. and Prince. M. J., Additive Effectiveness in Minerally-Enhanced Slurry Walls," *ASCE Specialty Conference on In Situ Remediation of the Geoenvironment,* ASCE Geotechnical Special Publication No. 71, October, 1997.

Evans, J. C., Adams, T. L. and Prince. M. J., "Metals Attenuation in Minerally Enhanced Slurry Walls," *Proceedings of the 1997 International Containment Technology Conference,* February, 1997.

Rowe, R. K., Quigley, R.M., and Booker, J. R. (1995) Clayey Barrier Systems for Waste Disposal Facilities. New York: E & Fn Spon,.

Risk-based selection of remedial measures for a shooting range area

U-M. Mroueh[1], E. Mäkelä[1], M. Wahlström[1], M. Olin[1], P. Vahanne[2], J. Liesivuori[3] & P. Kopponen[4]

[1]VTT Chemical Technology, P.O. Box 1403, FIN-02044 VTT, Finland
[2]VTT Communities and Infrastructure, P.O. Box 19041, FIN-02044 VTT, Finland
[3]Kuopio Regional Institute of Occupational Health, P.O. Box 93, FIN-70701 KUOPIO
[4]Department of Physiology, University of Kuopio, Snellmania, 70210 KUOPIO, Finland

Key words: Risk assessment, ecological effects, health risk, lead, heavy metals, remedial action scenario, encapsulation, reuse of sites

Malmi shooting range is situated in the northern part of Helsinki in the midst of residential and recreational areas. It was in use from 1937 until 1993. There were both bullet shooting and skeet and trap ranges in the area. There are plans to turn the site into a sports park and a recreational area. The south-eastern part of the area is reserved for residential houses, a school and a kindergarten.

Metal contamination of the site

An area of about 35 hectares is contaminated by lead pellets, bullets and dissolved metals. Several investigations of the site and its surroundings have been made with the aim of determining the extent and distribution of the contamination. The lead concentrations range from 100 mg/kg to 45 000 mg/kg. Concentrations over 5 000 mg/kg are found over extended areas. At the edges of the site the lead content falls to 100 - 300 mg/kg, which is at the level of background concentrations in Helsinki.

The pellets are partly degraded. The dissolved lead has been absorbed into the humus-containing surface layer (0 - 5 cm) of the soil. Minor concentrations of other dissolved contaminants, such as Cu, Zn, Sb, As and PAH, have also been detected. In the sectors with a high pellet content some lead was found in deeper soil layers and in the surface water. Increased metal concentrations were also found in ecological samples, such as mushrooms, berries, invertebrates and moles taken from these parts. The metal concentrations in the ground water did not exceed background values.

Risk assessment

The risk assessment was based on site-specific conditions. Potential exposure pathways and receptors were identified, and the exposures through the identified pathways were evaluated. Lead was selected as an indicator metal, because it was by far the most significant of the contaminants.

For the assessment of ecological risks, the analyses of samples taken from the site were compared with corresponding samples from other lead-contaminated sites, and with samples from traffic-contaminated background areas in Helsinki. Based on these comparisons and an extended literature search, it was concluded that mushrooms and earthworms are most sensitive to lead exposure, and may act as lead

carriers in the ecological food chains of the site. The background values of corresponding urban samples were significantly exceeded in the samples from those shooting range sectors, where Pb levels were > 300 mg/kg. It was concluded that, considering ecological risks, 300 mg/kg will be the concentration requiring remedial measures.

Humans using the site may be exposed to the contaminants through following routes:

- Ingestion of soil, especially by young children. The intake has been subject to a lot of discussion, and it is estimated to be 50 - 150 mg/day by various experts.
- Inhalation of lead-containing dust.
- Exposure from the intake of mushrooms and berries collected from the site.
- Exposure from drinking water is not possible under normal circumstances on the site. The potential spread of contaminants into ground water was, however, estimated by modelling.

There are no drinking water wells on the site, and the potential intake through inhalation is far less than that through ingestion of soil. Edible plants will not be grown on the site. Wild berries and mushrooms do grow in the wooded parts of the area and, if eaten, could cause adverse health effects. Their metal concentrations must be subsequently reduced to non-hazardous levels.

From the routes considered, ingestion of soil by children is the most significant. Young children are likely to frequent on a daily basis only those sites which are reserved for residential use. Those and nearby sites must be remediated to the levels that protect even pica children by removing the lead-containing surface layer. In the recreational area higher lead levels may be permitted because it is not likely that small children will spend much time in the area. In addition, the light, humus-containing surface soil will hardly be ingested by children in significant amounts.

Based on critical evaluation of the results of the human health assessment, it was concluded that in the surroundings of the residential areas, the soil containing over 100 mg Pb/kg should be covered. In the recreational area the remediation limit could be 600 mg Pb/kg, if only health risks are considered. Because of ecological risks, however, all the soil containing over 300 mg Pb/kg should be remediated.

Suggested remediation scheme

The area to be remediated is divided into two parts:

- Near the residential sites all the soil containing 100 - 300 mg Pb/kg must be covered with half a meter of clean soil.
- All the soil containing > 300 mg Pb/kg must be removed. The soil is planned to be encapsulated in accordance with the requirements for the landfill of hazardous waste. The containment system will be situated on the site, adapted to the architecture of the sports park. This solution was selected because it was almost impossible to find a site for the disposal of the soil outside the area.
- The sand from the catcher banks will be sieved. The lead-containing scrap is to be utilised and the sieved sand will be disposed into the containment system. Solidification of the catcher sand without sieving was also considered.

TRANSFER OF EXPERIMENTAL MEASURANDS FROM THE LABORATORY INTO THE REMEDIATION PRACTICE - COMPARARTIVE INVESTIGATIONS INTO THE BIOLOGICAL DEGRADATION OF CONTAMINANTS IN FIXED-BED REACTORS AND TECHNICAL REMEDIATION WINDROWS

M. Koning, K. Hupe, J.-C. Lüth, B. Lubitz, R. Stegmann

Department of Waste Management, Technical University of Hamburg-Harburg, Harburger Schloßstraße 37, D-21079 Hamburg, Germany
tel.: +49/40/7718-2438, fax.: +49/40/7718-2375, e-mail: koning@tu-harburg.d400.de

Key words: bio-piles, bio-reactor test, bioreactors, bioremediation, carbon balances, contaminated soil, hydrocarbons, microbiological soil remediation

SUMMARY
In comparative investigations the biological degradation of TPH (total petroleum hydrocarbons) in a middle distillate contaminated soil was observed in technical windrows and laboratory scale bioreactors. By creating optimized milieu conditions, the biological conversion processes in the laboratory test systems could be significantly accelerated compared to technical remediation windrows. This effect - in combination with an extrapolation of recorded measuring data - can be used to give an early prediction of the expected degradation of contaminants during a biological treatment of contaminated soils in technical windrows.

KURZFASSUNG
In vergleichenden Untersuchungen wurde der biologische Abbau von Mineralölkohlenwasserstoffen (MKW) in einem mit einem Mitteldestillat kontaminierten Bodenmaterial in technischen Sanierungsmieten und Laborbioreaktoren verfolgt. Durch die Einstellung optimierter Milieubedingungen ließen sich die biologischen Umsetzungsprozesse in den Labortestsystemen gegenüber den technischen Sanierungsmieten deutlich beschleunigen. Dieser Effekt kann genutzt werden, um in Kombination mit einer Extrapolation aufgenommener Meßdaten eine frühzeitige Prognose des zu erwartenden Schadstoffabbaus in einer Mietensanierung zu erstellen.

RÉSUMÉ
Dans des recherches comparatives, la dégradation biologique des hydrocarbures pétroliers dans un matériel de sol contaminé par un distillat moyen dans des tas d'assainissement et des réacteurs biologiques de laboratoire était observée. En ajustant des conditions d'ambiance optimisées, le processus de biodégradation pouvaient être accélérés considérablement dans les systèmes d'essai laboratoires en comparaison des tas d'assainissement techniques. Cet effet peut être utilisé pour mêttre une prévision tôt - en combinaison avec une extrapolation des données de mesure - concernant la dégradation expectée des substances pollutantes dans un assainissement en tas.

Contaminated Soil '98, Thomas Telford, London, 1998, 1091–1092

The transfer of experimental laboratory results into the remediation practice is a central problem in the biological treatment of contaminated soils. The time needed for the biological remediation, the effectiveness of conversion supporting measures and the purification success that can be expected by the treatment are quite difficult to assess in the remediation practice.

Within the scope of the research at the DFG-Research Centre SFB 188 'Treatment of Contaminated Soils', the effect of milieu conditions (oxygen content, water content) and organic additives (compost, bark) on the biological degradation of contaminants was examined in comparative investigations in fixed-bed reactors and in technical remediation windrows. The bioreactor tests were carried out in aerated fixed-bed reactors with a volume of 3l. To estimate the biological turnover of contaminants carbon balances were determined. While the milieu conditions in the laboratory test systems were kept constant (temperture: 20°C, water content: 36% soil field capacity, oxygen content: not limited), the milieu conditions inside the technical windrows varied spatially and changed over time (temperature: 20-45°C, water content: 33-55% soil field capacity, oxygen content: <1 - >20 vol.-%). Especially the limited oxygen content in larger parts of the windrows led on an average to a slower decrease in contaminants (see figure 1).

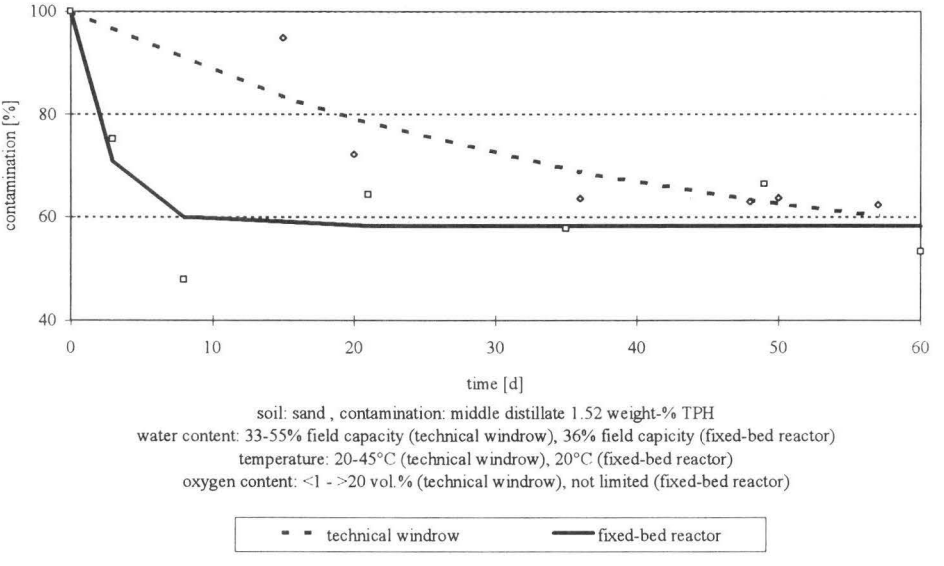


Figure 1: Decrease in contaminants in fixed-bed reactors and technical windrows

It turned out that the treatment period - until the plateau phase becomes apparent - could be significantly reduced in the fixed bed reactors. This effect - in combination with an extrapolation of measured data - can be used to give an early prediction of the expected degradation of contaminants in technical windrows.

CLEAN-UP OF HEAVY METAL POLLUTED SOILS: APPLICABILITY AND LIMITATIONS OF HYDROMETALLURGICAL TECHNIQUES

J. Thöming, H. Stichnothe, W. Calmano

Technical University of Hamburg-Harburg, Dept. of Environmental Technology
Eissendorfer Str. 40, D 21073 Hamburg e-mail: thoeming@tu-harburg.d400.de

Key words: chemical speciation, physico-chemical processing, electrolysis, extraction, leaching behaviour, heavy metals, sequential extraction procedure, thermodesorption

MOTIVATION

Heavy metals are one of the most challenging group of contaminants for soil remediation. Wherever they have ever been handled in the past, large areas with unacceptable high metal concentrations can be found as well as small amounts of soil bearing heavy metal salts up to several 10 % of dry weight. Especially for the latter case techniques are needed to treat excavated soil. Physico-chemical techniques offer the recovery of heavy metals in elemental form. They make use of hydrometallurgical unit operations which are well known in mineral processing. But in contrary to ores soils have a much more complex structure and a high variety of metal bindings restricting the applicability of those techniques.

There are two main tasks for such remediating processes:

1. separating completely the mobile metal fractions from the soil matrix and
2. keeping the used liquid in a closed loop avoiding waste water.

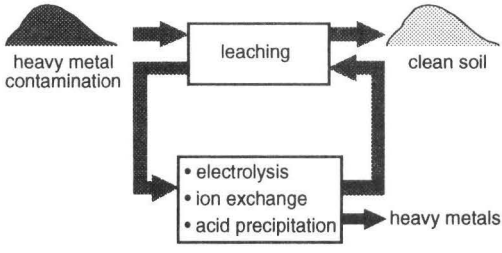


Fig. 1 Hydrometallurgical unit operations for a clean-up of heavy metal polluted soils

To what extend these tasks can be accomplished is shown exemplarily by two hydrometallurgical loop processes that make use of organic acids and sodium chloride, respectively. For assessing the applicability and the limitations of such processes metal speciation is needed.

EXPERIMENTAL

Before starting investigations for a clean up it has to be known how the metals are bound. Also after treatment the remaining amounts have to be quantified with respect to their binding forms or, at least, with respect to their mobile fractions. Here a sequential extraction scheme (which quantifies only operationally

Tab.1 Used sequential extraction

extr. a gent	*binding form*	*soil fraction*
NH_4NO_3	exchangeable	mobile
NH_4OAc	easily soluble	carbonates
NH_2OH-HCl	easily reducible	Mn-oxides
NH_4-EDTA	EDTA-extractable	organic material
NH_4-oxalate	moderately reducible	weakly crystaline Fe-oxides
ascorbic acid	strongly reducible	crystalline Fe-oxides
aqua regia	residual bound	residual

defined fractions) is used to assess the organic-acid-leaching of four different soils containing Pb, Zn, Cu, Cd and Sb in the range of 200 - 170.000 mg kg^{-1}.

A thermal desorption analysis is used to speciate elemental mercury of two soils containing 200 - 2000 mg kg^{-1} of Hg before and after treatment in an electrochemical hypochlorite-process.

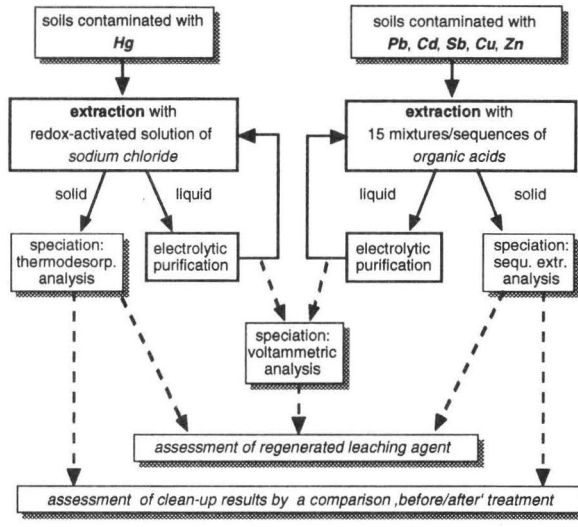


Fig. 2 Assessment of the applicability of two physico-chemical processes

RESULTS AND DISCUSSION

Although there are sophisticated 'Surface Complex Formation' models describing solid-liquid equilibriums clean-up results can hardly be predicted. These models assume the metal bindings being surface controlled, but this is not the case in real contaminations. Especially in soils that are highly contaminated there are own phases of precipitated metals forming small particles. This can be shown by instrumental speciation techniques [1]. In extraction processes these phases behave differently from surface bound metals and could lead to remaining 'mobile' amounts.

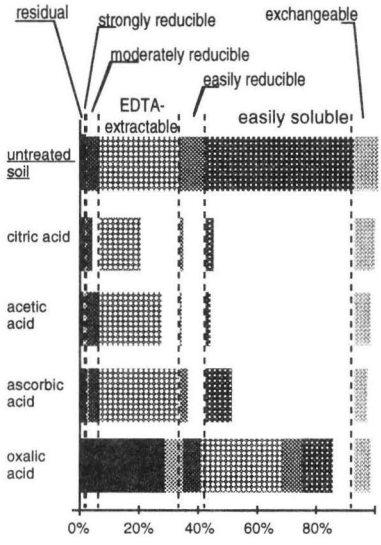


Fig.3 Cd-Distribution in soil fractions before and after treatment

It is shown in Fig. 3 that extractions with organic acids can lower total amounts in the range of 60 to 80 %. But even though, a total separation of mobile fractions can not be guaranteed. This limits the applicability of these processes and a great effort has to be undertaken to treat also highly contaminations sufficiently.

In the case of redox activated chloride extraction of mercury this problem is minimised because this process extracts up to 99,7% of the metal [2].

REFERENCES

[1] Welter, E., Calmano, W., Mangold S. (1998) First results of EXAFS-spectroscopy and SEM/EDX investigations on heavy metal contaminated soils as a tool for direct speciation analysis. This proceedings volume

[2] Thöming, J., Sobral, L., Wilken, R.-D. (1998) Electroleaching: A Mobile Clean Up Process for Mercury Contaminated Materials. In: Ebinghaus, Turner, Lacerda, Vasiliev & Salomons, Mercury Contaminated Sites. Characterization, Risk-Assessment and Remediation. Springer Environmental Science

Remediation and Rehabilitation of the Kuwait Oil Lake Beds

M. Iwabuchi[1], S. Kumamoto[1], Y. Shimizu[1], M. Asada[1], M. Sueyoshi[1], Y. Takano[1], N. Al-Awadhi[2], M. T. Balba[2], R. Al-Daher[2]

[1] Shimizu Corporation; Shibaura 1-2-3, Minato-ku, Tokyo 105-07, Japan
[2] Kuwait Institute for Scientific Research, P.O.Box 24885, 13109 Safat, Kuwait

Keywords; contaminated soil, environmental impact, field experiment, hydrocarbons, in-situ remediation, oil-products, physico-chemical washing process, sludge/slurry, solvents

Introduction

The destruction of oil fields in Kuwait during the Gulf War resulted in unprecedented large scale environmental damage : an estimated 50M barrels of crude oil spilled into lower areas of the desert forming hundreds of oil lakes, contaminating roughly 23M m^3 of soil (Fig.1) and threatening precious ground water resources.

In 1994, in collaboration with the Kuwait Institute for Scientific Research (KISR) and in cooperation with the Kuwait Oil Company (KOC), Shimizu began the ongoing joint research programme of "Remediation and Rehabilitation of the Kuwait Oil Lake Beds."

The programme is sponsored by the Petroleum Energy Center (PEC) of Japan, under the auspices of the Ministry of International Trade and Industry of Japan.

One of the primary goals of the programme is to develop a physico-chemical treatment technology for the oil lake beds. The programme has included a technology review, site surveys, and laboratory and bench-scale tests. Based on data collected from such work, a pilot plant was constructed in the Burgan Oil Field in Kuwait in 1996.

Oily Sludge

The most heavily-contaminated portions of the oil lake beds consist of sedimented oily sludge. The sludge contains on average, 50w% crude oil, 20w% salt, and 30w% sand. The high level of salinity attributed to the large quantities of seawater used for extinguishing well fires following the War. While salinity levels remain relatively consistent regardless of the depth of sludge, oil and sand content vary. Surface sludge contains more oil, 60w%, and less sand, 20w%, while bottom sludge contains less oil, 30w%, and more sand, 50w%. Furthermore, the lighter elements of oil have evaporated from the sludge due to the severe distillation effect of sunshine. As a result the sludge is extremely viscous. Application of solvent and heat allow for easier handling of such sludge.

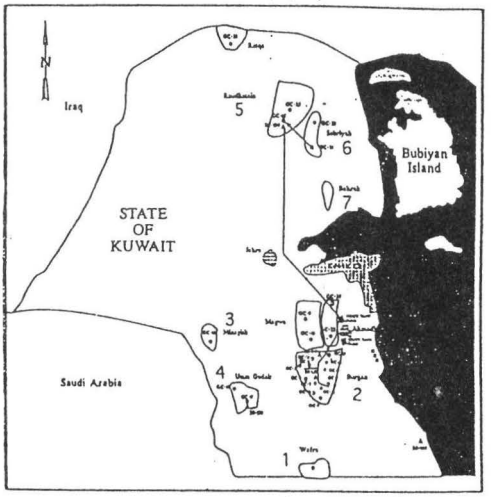


Fig.1 Oil Lakes In Kuwait

No	Oilfield	Contaminated Area(km^2)	Contaminated Soil(m^3)
1	Wafra	3.3	1,956,000
2	Burgan	25.6	14,520,000
3	Minagish	0.2	95,000
4	Umm Gudair	0.3	135,000
5	Raudhatain	12.3	2,456,000
6	Sabriya	6.9	3,083,000
7	Bahra	0.7	408,000
	Total	49.3	22,653,000

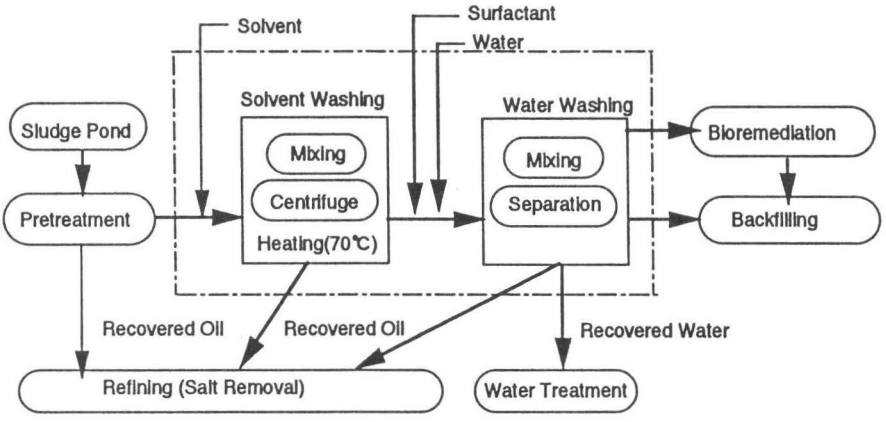


Fig.2 Flow Diagram of Soil Washing Process

Soil Washing Process

The developed treatment process (Fig.2) combines solvent washing and water washing of oily sludge at a temperature of 70℃. There is a pretreatment unit for heating, crushing and loading sludge, and wastewaer treatment unit for separating oil and evaporating water.

The process has successfully reduced oil and salt contents of oily sludge, resulting in treated soil at environmentally acceptable levels. On average, the process has achieved oil reduction from 50% to 4% and salinity reduction from 20% to 2% (Fig.3).

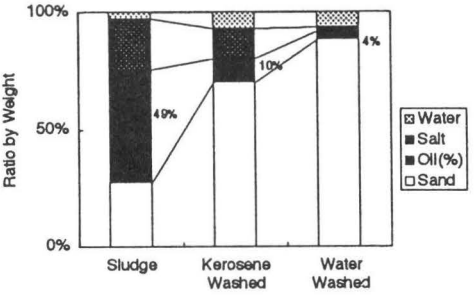


Fig.3 Oil Reduction by Washing Process

Salt Removal from Recovered Oil

During the washing process, significant amounts of oil are recovered. However, the high salinity levels existing recovered oil must be reduced before it can be used as fuel. Additional utilization of heat, solvent, water and emulsion breaker in an ancillary process (Fig.4), reduces such salinity from 20w% to 800ppm.

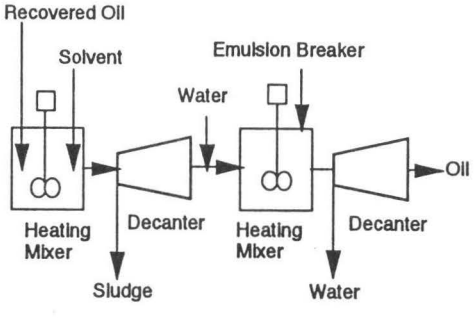


Fig.4 Flow Diagram of Recovered Oil Refining

AN IN-SITU REACTIVE BARRIER FOR THE TREATMENT OF GROUNDWATER CONTAMINATED WITH TRICHLOROETHENE: CONSTRUCTION AND OPERATIONAL PERFORMANCE

A.O. Thomas[1], D.G. Haigh[2], M. Roper[2], S.A. Jefferis[3] and G. Norris[4]

[1] Golder Associates Geoanalysis s.r.l., Via A. Banfo, 43, 10155, Turin, Italy
[2] Golder Associates (UK) Ltd., Edwalton, Nottingham, NG12 4DG, U.K.
[3] Golder Associates (UK) Ltd., Maidenhead, Berkshire, SL6 8BN, U.K.
[4] Nortel, Oakleigh Road South, New Southgate, London, N11 1 HB, U.K.

Key words: in-situ groundwater remediation, reactor, barriers, trichloroethene

SUMMARY

The use of zero valent iron for the treatment of chlorinated solvent groundwater plumes is a promising alternative to long term containment using established technologies such as pump and treat. The conceptual design and laboratory evaluation of the technology to treat a trichloroethene (TCE) plume in Belfast, Northern Ireland has previously been reported [(1)]. The challenges posed by the construction of the full scale system and the operating performance of this first UK and European reactive wall are the subject of this presentation.

Laboratory and modelling studies indicated that a relatively long pathlength was required to completely reduce the chlorinated solvents. The proximity of the site boundary negated this possibility. In response, Golder Associates devised a reaction vessel concept that elongated the reactor's pathlength by diversion vertically through a cylindrical column of iron filings, resulting in a final column of some 12 m in length. Groundwater is collected using a funnel positioned approximately perpendicular to the flow path. The funnel was created by placing a cement-bentonite wall in a V shape to a depth of around 12 meters. The reactor was situated at the apex of this wall to act as the permeable reactive gate. Reactor sand piles were then located at points downstream and upstream. Arms from the reactor vessel were pushed into these sand piles to form the collection and distribution arms.

Monitoring results on the device installed early in 1996 have been very encouraging. Monitoring has been performed around the reactor by taking samples from upgradient and downgradient wells in addition to sampling form 5 sampling points within the reaction vessel. Analysis included major ions, TCE and degradation products as well as iron and manganese.

Upgradient wells have shown fluctuations in concentration which may be due to seasonal variation in water level resulting in differential dissolution of free product. A general reduction in concentration is however, superimposed over this behaviour since the reactor was installed.

Monitoring wells downgradient of the reactor also show this fluctuation. These wells have also shown a reduction in TCE concentration since the reactor began service.

Contaminated Soil '98, Thomas Telford, London, 1998, 1097–1098

Monitoring within the reactor shows clear evidence of the elevated TCE levels upgradient of the reactor being reduced as flow through the reactor occurs. Data shows a 99.97% reduction in TCE levels and daughter products through the reaction vessel.

The iron filings have created a strongly reducing environment instigating reductive dechlorination of the chlorinated solvents, thus producing chloride and chlorine free hydrocarbons. The effectiveness of the reactor can be observed from the increase in chloride concentration downgradient compared to the upgradient wells, indicating dechlorination is occurring.

In addition to the positive results, the reactive treatment system offers many benefits in comparison to other methods. The technology requires no power input and can be installed in remote areas, operating costs are minimal, there are no effluent treatment costs and all chlorinated solvents are treated. Further, it is estimated that the overall cost of this system is around 25% to 33% of the installation costs for an extraction system which would have had to run for a number of years.

(1) Thomas A.O, Drury D.M., Norris, G., O'Hannesin S.F., and Vogan J.L., 1995. The in-situ treatment of TCE contaminated groundwater using a reactive barrier - Result of Laboratory Feasibility studies and preliminary design considerations. In : Contaminated Soil 1995, Proceedings of 5th KNK/TNO Conference held at Maastricht, Netherlands, W. J. van den Brink, R. Bosman and F. Arendt (eds.), Kluwer Academic Publishers. Netherlands. pp. 1083 - 1091.

IMMOBILIZATION OF SOIL: FROM CO-DISPOSAL TO BENEFICIAL USE

J.L.M. van Leeuwen and A.H.M. Pepels

Gemeentewerken Rotterdam (Public Works) Department of environmental engineering; P.O. BOX 6633, 3002 AP ROTTERDAM;

Keywords: immobilization, soil, cyanide, leaching

1. Introduction

In the city of Rotterdam large quantities of contaminated soil are excavated each year. In case the soil is non cleanable, it has to be disposed of in an isolated and controlled landfill. At the landfill the contaminated leachate has to be purified on the long term. Especially cyanide is a problem in the leachate as complexes of cyanide are mobilized after excavation, as a result of the contact with oxygen and light.
The policy of Rotterdam aims at the stimulation of beneficial use of contaminated soils. By using immobilization as a treatment technique, the opportunitions for leachate control or, even better, beneficial use are improved.

2. Methods and materials

Public Works Rotterdam has studied the feasibility and implementation of immobilization of contaminated soils. So far two approaches have been studied:

1) beneficial use of sandy soils, contaminated with heavy metals, pah's and/or other contaminants.
   -adding of cement
2) co-disposal for cyanide contaminated soils
   -adding of or mixing with sediments, cement, bitumen

The immobilized soils have been tested on both physico-mechanical and environmental aspects. The compressive strength after 28 days and after freeze/thaw and wet/dry cycles and the leaching of contaminants in the tank leaching test (NEN 7345) has been compared to Dutch standards.

3. Results

The first track (beneficial use) has resulted in a full scale demonstration project, in which contaminated soil has been immobilized with cement in a road base (ref. 1). The results are in accordance with Dutch standards.
The conclusions of the project are:

- The leaching of heavy metals is in accordance with Dutch standards. The base seems environmentally safe and no isolating provisions are required.
- The compressive strength is sufficient according to the standard of 1.5 N/mm^2. The spreading in the results is equal to those of sand-cement stabilizations. The sustainbility is judged good.
- Considering the costs of landfilling, a minimum batch size of 500 tons of soil is economical beneficial, when it is immobilized.

Contaminated Soil '98, Thomas Telford, London, 1998, 1099–1100

- The site, including its base, is still in use, and no problems are being encountered.
- In future projects a critical review on the optimal content of cement is recommanded. The results of standardized tests in a laboratory with each batch of soil are preferable to the use of the empirical relation of the water-cement ratio.
- The need for licences and an environmental impact assessment, in the Netherlands, will cause problems for the on-site immobilization of hazardous materials in constructions.

The second track (co-disposal) has lead to some hopefull results, on a lab scale, which can be used in soil-sanitation and landfill maintenance discussions. The study consisted of modelling of chemical equilibria (speciation) and column experiments. The speciation of cyanide in the soil determines strongly the leaching. By lowering both pH and redoxpotential of the soil, the speciation of cyanide can be changed into an immobilized form, leading to immobilizaton in a chemical way.
By adding of or mixing with sediments the leaching of cyanide can be reduced as sediments both influence pH and redoxpotential. Co-disposal with contaminated sedimentents can be an interesting option at disposal sites. The adding of cement to cyanide contaminated soil leads to a concrete like product, which has possibilities for beneficial use in road constructions. However, the addition of cement or bitumen seems not to reduce the leaching below Dutch leaching standards. In this way only a fysical immobilization takes place.

4. Conclusions

Immobilization gives new opportunities for non cleanable soil. A distinction has to be made between cyanide and heavy metal/pah's contaminated soil.
As excavation leads to mobilization of cyanide, it is discussed whether to excavate or not when the soil can't be cleaned. In-situ isolation, co-disposal or partial cleaning has to be studied carefully, regarding changes in pH and redoxpotential and the influence on the speciation of cyanide.
The demonstration project has shown that it's possible to use immobilization as technique for metals and pah's contaminated soil, on a full scale. Immobilized contaminated soil, that otherwise should have been disposed of, can be used in infrastructural works.

4. References

1) Leeuwen J. van, A. Pepels and G. van Emst. *Contaminated soil - cement stabilization in a demonstration project. Waste Materials in construction, Putting theory into practice.* J.J.J.M. Goumans *et al*, Proceedings of WASCON'97, Elsevier 1997, pp. 815-822.

THERMAL TREATMENT OF CONTAMINATED CATCHER-SAND FROM FIRING RANGES

Ir. H.H.A.G. Wevers — DHV Environment & Infrastructure, P.O. Box 1076, NL-3800 BB, Utrecht, The Netherlands

Ing. Th.J. Kramer — Dutch Ministry of Defence (DGW&T), P.O. Box 90027, NL-3509 AA, Utrecht, The Netherlands

Keywords — Thermal treatment, Soilremediation, Recycling, Reuse, Heavy metals, Firing range, Catcher-sand

Introduction

The Dutch Ministry of Defence currently manages about 150 firing ranges at 40 different locations (both in use and out of use). After a period of use the bullet catcher-sand (i.e. the sand in the hill behind the targets which catches the projectiles) becomes strongly contaminated with heavy metals (primarily lead, but to a lesser degree copper, zinc and antimony). Contaminated catcher-sand is removed from the firing range at the moment potential risks to public health (personnel) arise, such as the danger of ricochet (through the formation of so-called lead balls as bullets collect) and the presence of polluted dust.
According to the current international standards, the removed catcher-sand must in many cases be classified as a dangerous substance (containing more than 5,000 ppm of lead). The processing of this sand has presented considerable challenges.
The Dutch Ministry of Defence has conducted a study into the development of an effective and economic processing method for the catcher-sand. In accordance with the Ministry's environmental objectives, emphasis was hereby placed on high quality reuse and a positive impact on the environment.

Characterisation of the contamination

The key to the development of an effective processing method has lain in a thorough and accurate characterisation and analysis of the contamination in the matrix of the catcher-sand. In addition to the specific presence of coarse (bullet) shell debris (larger than 2 mm), it is essential to realise that the catcher-sand is contaminated differently than 'genaral cases of heavy metal contaminated sand'. This came to light after a number of trial cleaning attempts using extraction methods in which the expected results were not achieved, and through scientific research which has been carried out by the University of Technology (TU) of Delft.
According to the research at TU Delft it appeared that the lead is not (as is usual) solely concentrated in/on the fine fraction and/or absorbed into organic substances, but spread over all grain-size fractions. The cause of this is the formation of a lead coating surrounding the grains of sand. On entering the sand hill, a shell or bullet must expend an enormous amount of kinetic energy in a very short time. During deceleration of the projectile by the sand (and to a lesser degree by air resistance during flight), a very high degree of friction energy is created which is converted into heat that 'melts' the outside of

the projectile. As it enters the sand pile, this 'liquid' lead spreads over all the grains of sand it comes into contact with. Because the driving force of the bullet breaks sand grains along minuscule faults, even the very fine sand grains can also be coated with lead. This contamination mechanism was shown by the TU Delft research, by means of an electronic microscope, among other analysis methods.

Processing method

After comparing several processing methods, the use of the projectile catcher-sand in the metal (lead ore) processing industry was indicated as the best choice. After orientation at a number of foreign companies (in the Netherlands no large-scale lead production industry is present) and after a trial processing of 500 tons, a contract was signed with the company Union Minière (UM), in Hoboken, Belgium.

The processing of lead ore into lead and other metals at UM is carried out in a smelting process. In the blast furnaces the lead ore and additives are melted together, producing 'raw' metallic lead (main product) and a slag.
The input of the melting process at UM consists mainly of sinter (ore and additives). The sinter must have a very precise composition for accurate process control. Approximately 10% of the sinter should consist of SiO_2, which is added in the form of sand, which in turn consists of 85-95% SiO_2. In the past this sand was supplied by dredging the river Schelde. In the context of this project this dredged sand has now largely been replaced by catcher-sand. By processing the catcher-sand by UM the largest part (80-95%) of the heavy metals in the catcher-sand are retrieved and processed into end products (pure metals). This is, therefore, a form of high-quality metal recycling.

Conclusions

The major arguments in support of processing catcher-sand at UM are:

1. The large majority of all heavy metals present in the catcher-sand are recycled;
2. The very fine residual metalfraction in the catcher-sand, which can not be recycled, is immobilised thermally, at the same time creating a re-usable (building) material;
3. The sand (silicon oxide, which makes up more than 85% of the catcher-sand) is used as an aid in the lead smelting process;
4. UM will not (or only slightly) have to adapt its production process;
5. UM possesses all necessary (environmental) permits and is regularly inspected by the Public Waste Company for the Flemish District (OVAM);
6. The processing costs are lower than the costs of disposal of the catcher-sand.

Since the start of the project, over 17,000 tons of catcher-sand have been processed by UM. The processing has been successful and has not led to insurmountable problems in the areas of process technology, logistics or technical permits. In principle, only projectile catcher-sand is eligible for this processing method because the sand must meet the stringent quality requirements of UM. It can be concluded that the Ministry of Defence is successfully processing heavily contaminated catcher-sand using a unique processing method.

Off-site bioremediation of contaminated soil and direct reutilization of all soil fractions

K.- H. Robra, W. Somitsch, K. Becker, J. Jernej, M. Schneider and A. Battisti

Institute for Environmental Biotechnology, Graz University of Technology, Petersgasse 12, A-8010 Graz, Austia

Key words: Mineral oil hydrocarbons, mixed population, fluidized-bed reactor

Soils contaminated with mineral oil hydrocarbons can be cleaned by microbiological remediation techniques. The degradation of a hydrocarbon mixture of refined oil requires the combined activities of several different microbial populations[1]. Adaptation of microbial communities to hydrocarbons was enriched from oil contaminated soil, suspended in a mineral salt medium with the final pH of 7.5. The mixed population is characterized by the immobilization of the microbial cells by adhesion at the soil particles.

The process flow with the technical equipment for the aerobic biodegradation of mineral oil hydrocarbons operates according to a process scheme that includes the processing stages of pre-treatment, soil separation unit for the wet liberation and sizing with a completely closed waste water circuit (Fig. 1). For wet liberation and sizing, the soil was transferred into the separation unit and mixed with water without addition of chemical reagents. The mechanical separation aims at a dispersion of agglomerates to release and to suspend pollutant particles. As the result of the wet treatment and the separating processes, the suspension of the fine soil with a particle size fraction of ≤ 500 µm and a share of ≤ 30% is discharged from gravel and transferred with a slurry pump into the bioreactor. The slightly contaminated gravel fractions are washed separately with fresh water and subsequently dewatered. The process water is fed back into the water circuit. The exhausted air from the bioreactor containing volatile hydrocarbons is led through an activated carbon filter and cleaned.

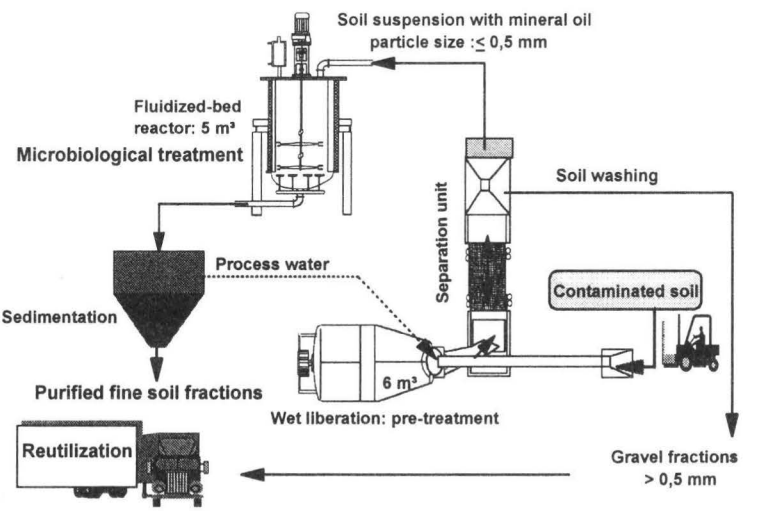


Figure 1 Process flow for aerobic off-site bioremediation of contaminated soil

The clean-up operations were carried out in a semi-continuous fluidized-bed reactor at 30° C, with a volume of 5 m^3 and a final soil concentration of 30% (w/v) with a particle size ≤ 500 µm. Concentrations of 2g - 12 g oil hydrocarbons by kg soil were mineralized in soil within 14 hours, and addition nitrogen to aerated soil prolonged the rapid phase metabolism (Fig. 2). The concentration of oil hydrocarbons in the soil decreased clearly when the immobilized microorganisms started growing. The measurement of oxygen consumption rate during the time of incubation characterizes the growth and the catabolic activity of the mixed population until the decreased substrates becomes the limiting factors. The rate of biodegradation of mineral oil hydrocarbons was determined in samples of the treated soil with average values from 200 mg/kg. The analytical data suggest that sorption of mineral oil hydrocarbons may have a major impact on the rate of degradation by microorganisms. Identification and quantification of the oil hydrocarbons were achieved by using a gas chromatograph equipped with a flame ionization detector [2].

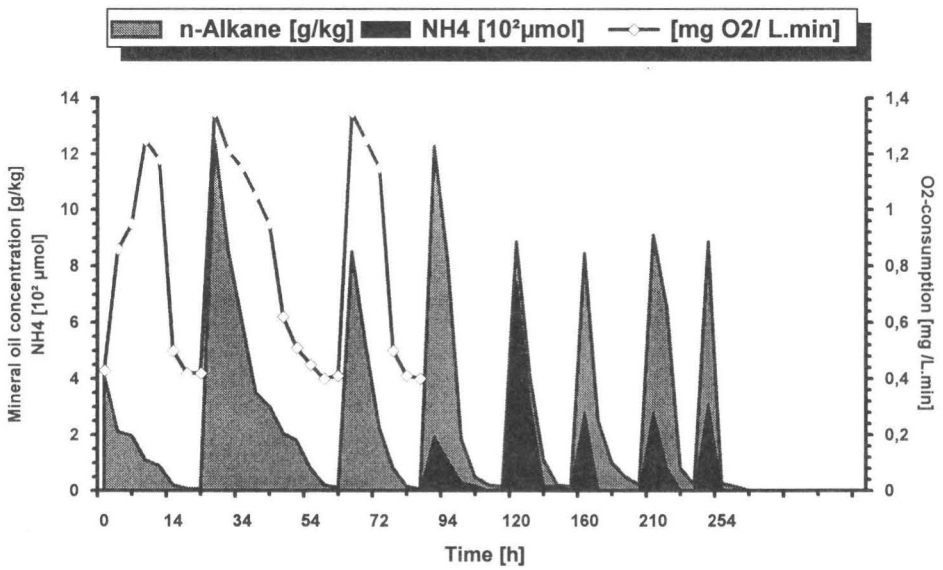


Figure 2 Semi-continuous degradation of mineral oil by immobilized mixed population

The combination of physical adsorption and biological degradation of oil hydrocarbons seems to be applicable for the treatment of soil decontamination. The aim of decontamination and biodegradation is the reutilization of the soil and the reduction of environmental risks resulting from migration of contaminants.

REFERENCES

[1] Atlas, R.M. and Bartha, R. (1992) Hydrocarbon biodegradation and oil spill bioremediation. Adv. Microbial Ecol. 12, 287-238.

[2] Somitsch, W., Jerney, J. and Robra, K.-H. (1994) Quantitative analysis and characterization of mineral oil contaminated soil by GC-data processing. Fresenius Envir. Bull. 3, 358-364.

GREEN SOIL CLEAN-UP BY FARMERS: A CHALLENGE?

Peter C. Leendertse and Gé A. Pak, Centre for Agriculture and Environment (CLM), P.O. Box 10015, 3505 AA Utrecht, The Netherlands.

Key words: agriculture, clean-up, contaminated soil, phytoremediation, heavy metals.

SUMMARY
There are a number of "green soil clean-up" measures which can be carried out by farmers to deal with contamination of their agricultural soil.

INTRODUCTION

A part of the agricultural land in Europe is contaminated with heavy metals or organic micropollutants (Stanners and Bordeau 1995). The agricultural acreage contaminated with heavy metals in The Netherlands is estimated at more than 100,000 ha, about 5% of the total agricultural acreage (Weckseler et al. 1995). Contamination of agricultural land presents problems for farmers: It is not clear if current farm management can be continued and if anything can be done about the contamination. Furthermore the risk of production restrictions may make farmers wary of reporting contamination. A clear and especially stimulating policy is needed, aiming at cleaning up or controlling contaminated plots.

APPROACH

CLM developed a strategy in which farmers carry out the relevant measures to control or clean up contamination themselves whenever possible. The strategy is called "green soil clean-up" and consists of both technical measures and financial/organisational support. In this study the suitability of technical measures for use in contaminated rural areas has been assessed. Both environmental and agricultural criteria have been used for this assessment.

RESULTS

Three different groups of possible measures have been recognized:
1) removal of contaminants 2) control of harmful effects of contaminants 3) prevention of harmful effects of contaminants.

The type of measure depends on the level of contamination. For contamination of agricultural soil three groups of contamination can be discerned depending on so-called warning values for agricultural soils. These values do not have a legal status, but they are an instrument in determining whether a contaminated plot is still suitable for agriculture. The type of measure which is most useful for a contamination and which can be carried out by farmers is illustrated by a decision tree (Figure 1).

1)*Removal* of contaminants is advised if the contamination is above the agricultural warning value and poses a risk for crops or animals. Only phytosanitation, the removal of heavy metals by using (hyper-)accumulating crops, appears a suitable removal method for farmers. One example is the cultivation of rape seed on agricultural soil with a contamination above the agricultural warning value for cadmium. Using this cultivation a farmer can reduce the cadmium content of his soil below the warning value in six years (Table 1).

Cd in soil	Cd agricultural warning value	Cd to be removed (X)	biomass rape seed	Cd in biomass	yearly removal (Y)	removal time (X/Y)
9.0	7.2	1.8	10,000	30	0.3	6

Table 1: Theoretical removal time (years) of cadmium (kg/ha) by cultivation of rape seed (kg/ha) by farmers

Contaminated Soil '98, Thomas Telford, London, 1998, 1105–1106

2) *Control* of contaminants is advised if the contamination is above the value but without a direct risk for crops or animals. Control is possible by breaking down the contamination by biological decontamination (e.g. PAH's), by diluting the contamination by means of deep tillage or by fixing the contamination by means of liming, increasing the organic matter content or by introducing substances into the soil which bind the contamination (Figure 1).

3)*Prevention* of harmful effects of contaminants is advised if the contamination is below the agricultural warning value. A reduction of the use of inputs containing contaminants (chemical fertilizers, pesticides) is the main prevention measure.

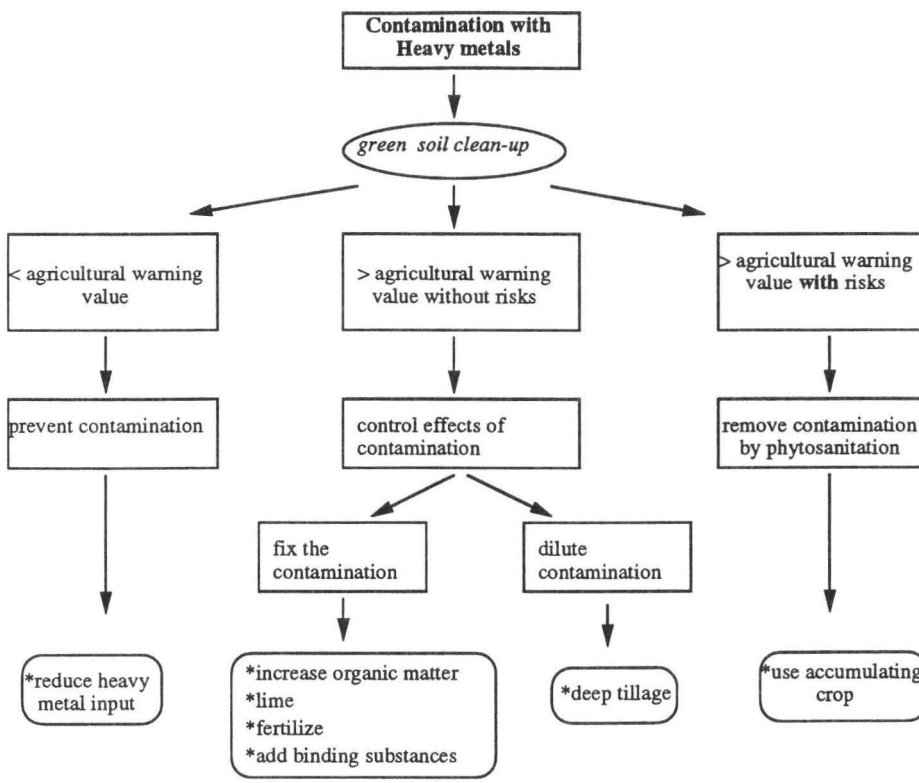


Figure 1: Decision tree for green soil clean-up of heavy metals by farmers

CONCLUSION

It can be concluded that there are a number of measures which can be carried out by farmers to deal with contamination of their agricultural soil. It is recommended to further develop the technical measures and to create a financial and organisational framework for green soil clean-up. Successful development of the green soil clean-up is a challenge to farmers, researchers and policy makers.

REFERENCES

Stanners, D. and P. Bordeau (1995). *Europe's environment. The Dobris assessment*. European Environment Agency, Copenhagen.

Weckseler, H.J. , M.C. Hanegraaf and G.A. Pak (1995). *Groene bodemsanering*. Centrum voor Landbouw en Milieu, Utrecht.

AIR AND CONTAMINANT MIGRATIONS IN GROUNDWATER INDUCED BY IN-SITU AIR SPARGING

T.Hirata[1], N.Egusa[1], K.Fukuura[2] and T.Matsushita[2]

[1] Dept. of Environmental Systems, Wakayama Univ. ,930 Sakaedani,Wakayama 640-8510, Japan
[2] Maezawa Industries Inc. , 5-11 Nakamachi, Kawaguchi 332-8556, Japan

Key words: in-situ air sparging, volatile organochlorines, air migration

INTRODUCTION

The volatile organochlorines are strongly persistent to biodegradation in subsurface environment, therefore, various sorts of remediation technologies are developed and applied to remove the contaminants. Among them, in-situ air sparging depends on air injection and aeration in contaminated groundwater, thereby it can be a cost-benefit technology which needs only extracted soil vapor treatment without pumping groundwater up. The in-situ air sparging technology was applied to a site contaminated with volatile organochlorines like tetrachloroethylene, carbon tetrachloride, chloroform etc. which were utilized to produce agricultural chemicals for many years.

FIELD TEST

In order to clean up the shallow groundwater, the in-situ air sparging system using air injection and soil vapor extraction wells was employed. Figure 1 shows DO(dissolved oxygen) concentration in groundwater as an indicator of injected air migration route. The vertical scale is measured from the shallow groundwater table, and the air injection well at the bottom of the figure is located at the distance of 6m away from the extraction well. The DO concentration pattern after Run 3 air sparging (see Figure 2) was made using nine monitoring wells of Md51 through Md83, the locations of which were indicated as the closed circles and existed in a same section. The DO concentration pattern shows not uniform but parabolic rise from the injection well due to the balance between the injected air pressure and buoyancy force in groundwater. In addition Figure 2 illustrates time varied changes of tetrachlroethylene concentration in groundwater at nine monitoring locations as shown in Figure 1. The figure also shows the periods of air injection of Run 1 through Run 4, and Run 3 corresponds to Figure 1. The volume of air injected from one injection well amounts to 120 L min^{-1} and the extraction volume of soil vapor is up to 150 L m^{-1} in. During the periods of Run 1 and Run 2, the air sparging system was under operation using an injection well and a soil vapor extraction well, both of which are placed at the same location of being the lateral origin Figure 1. The air injection reduces the tetrachlofoethylene concentrations of Md52 and Md53, which are 1.5m away from the injection well. In particular during the periods of Run3 and Run 4, in which the injection and extraction wells at the different location were utilized as mentioned above, the tetrachloroethylene concentrations of Md72, Md73 and Md81 depict a sharp decline, while those of Md82 and Md83 keep nearly similar or rather high level prior

to the operation of Run 3. Such difference between the time varied changes of tetrachlofoethylene concentration at monitoring wells is consistent with the injected air migration pattern in groundwater as displayed in Figure 1.

CONCLUSIONS

The influence radius of sparging air and change of contaminant concentration due to air sparging technology could be understood based on the results of a field test. And also an available information for establishing in-situ air sparging technology was obtained. The authors will evaluate the full scale remediation using the air sparging system by field measurement and numerical simulation.

ACKNOWLEDGEMENT

Some of this study was performed using funds from the Nippon Life Insurance Foundation.

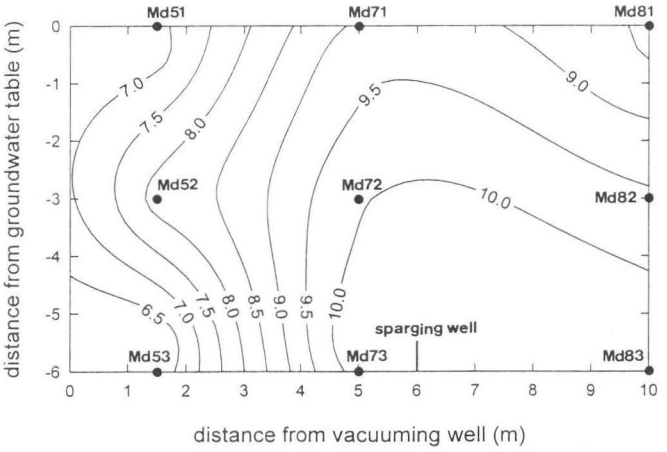


Figure 1 The DO concentration pattern in groundwater induced by air injection into contaminated groundwater.

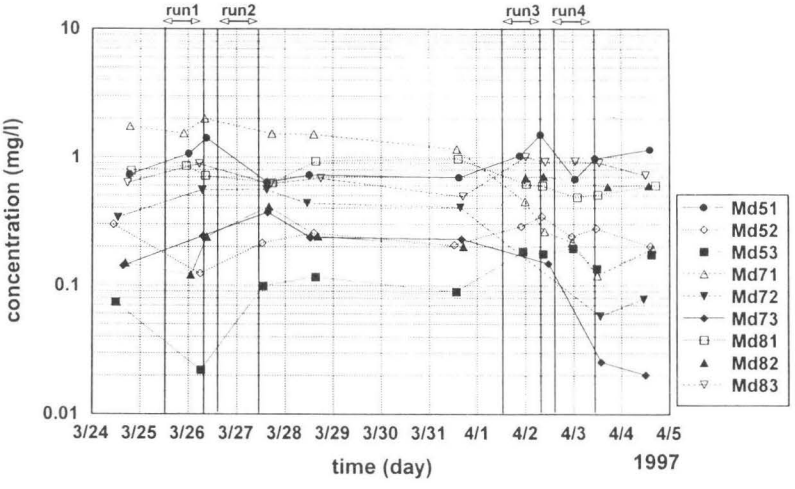


Figure 2 Time varied changes of tetrachloroethylene concentration observed at nine monitoring wells in Figure 1.

ASSESSMENT OF SOIL QUALTITY USING A MULTITIERED TEST BATTERY OF BIOASSAYS

J. Bierkens [1], G. Klein [1], P. Corbisier [1], R. Van Den Heuvel [1], L. Verschaeve [1], R. Weltens [1], G. Schoeters [1].

[1] Flemish Institute for Technological research - VITO, Boeretang 200, 2400 Mol, Belgium.

Key words: Bioassays, biomonitoring, contaminated soil, quality of soil, risk analysis, toxicity tests

At present risk assessment of contaminated soils is mainly based on chemical analyses of a priority list of toxic substances, corrected for the total amount of organic and inorganic matter in the soil. This analytical approach does not allow for combination toxicity, nor does it take into account the bioavailability of the pollutants present. In this respect bioassays provide an alternative because they provide a measure for the environmentally relevant toxicity, i.e. the effects of a bioavailable fraction of interacting pollutants set in a complex environmental matrix. However, increasing evidence suggests that the use of a single bioassay will never provide a full picture of the quality of the environment, i.e. that only a testbattery, composed of bioassays on different species from different trophic levels will contain sufficient discriminatory power to allow assessment of the quality of the environment.

In the present study, a testbattery composed of 20 bioassays probing for different biological endpoints in different animal and plant species has been compared. Apart from lethality and reproductive failure in earthworms, springtails, nematoda, algae and vascular plants, these endpoints also included bioavailibility of metals (bacteria), heat-shock induction (nematodes, algae), DNA damage (bacteria, earthworm, vascular plants), β-galactosidase (Daphnia) and esterase activity (algae) and a range of immunological parameters (earthworm). Four chemicals i.e. cadmium, phenol, pentachlorophenol and trifluralin - each representing a different toxic mode of action - have been applied in a dilution series (from 1 mg/kg up to 1000 mg/kg) unto OECD standard soil. The tests have been performed both on these artificially contaminated soil samples and on aqueous extracts subsequently obtained from these soils.

As previously shown at the species level, no single biological endpoint was shown to be the most sensitive for all four modes of toxic action. Whereas the immunological parameters and the loss of weight in the earthworms were among the most sensitive solid-phase assays (Figure I), esterase inhibition and heat-shock induction in algae were shown to be extremely sensitive when applied on the soil extracts (Figure II). Some caution in interpreting these relative sensitivities should be taken since only four modes of toxic action have been included in this study. As such, aspecific biological endpoints (e.g. heat-shock proteins) tend to be favoured over more specific testsystems (e.g. genotoxicity). It should be kept in mind however that in order to obtain a well-balanced testbattery these more specific bioassays should not be omitted.

Figure I: Relative sensitivity of solid-phase bioassays (w = LOECx/LOECaverage).

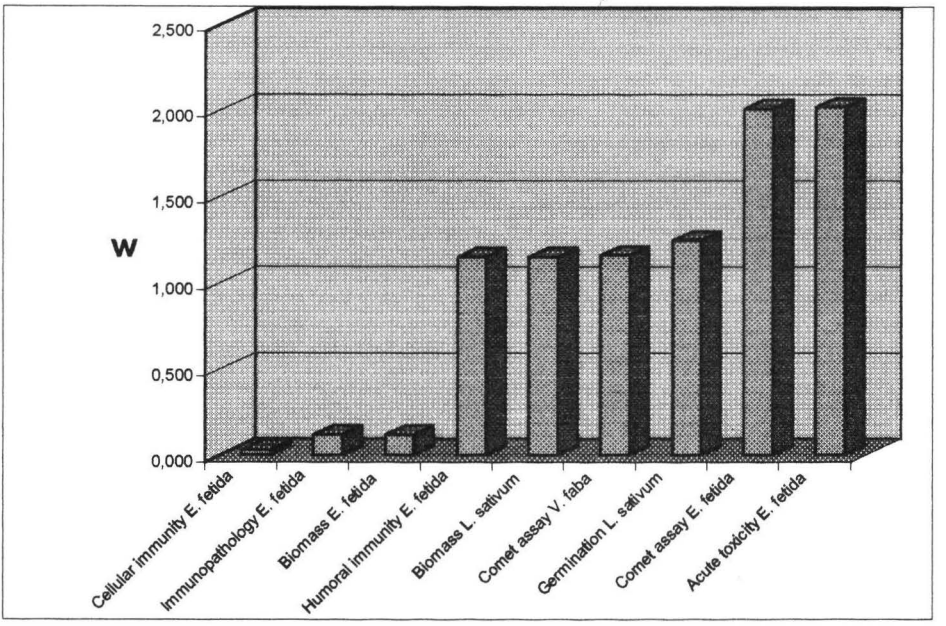
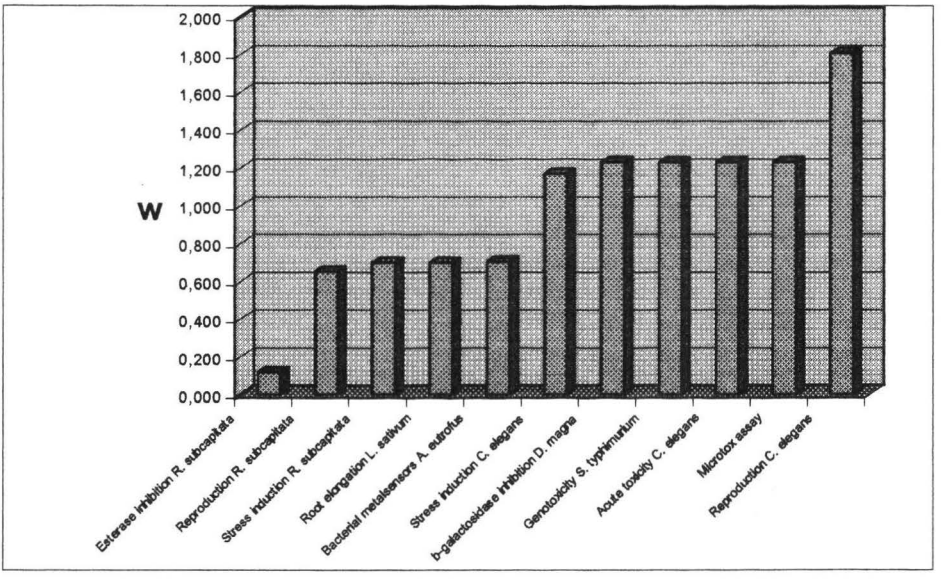


Figure II: Relative sensitivity of bioassays performed on soil extracts).



Soil remediation by metal-accumulating plants: how to monitor the success of remediation?

Armin Keller, Berchtold von Steiger, Achim Kayser and Rainer Schulin
Soil Protection, Institute of Terrestrial Ecology, ETH Zürich
Grabenstr.3, CH-8952 Schlieren, Switzerland
http://www.ito.umnw.ethz.ch

Key Words: monitoring, soil remediation, heavy metals, contaminated soil, spatial variability, plants

Introduction: Increasing pollution of cultivated soils, e.g. agricultural land, gardens etc., requires remediation measures. Decontamination of such soil should maintain the soil fertility. An emerging technique for soil remediation is the extraction of heavy metals by metal-accumulating plants.

Monitoring the success of remediation requires planning and controlling of the contaminant fluxes. This should be based on mass flux balances of the contaminants considering spatial and temporal variability on the field scale as well as on the regional scale. The main flux to focus on is the heavy metal pathway soil plant which depends largely on plant species, biomass production, heavy metal element and degree of metal contamination in soil, degree of heavy metal bioavailability (chemical and physical soil parameters), cultivation techniques and climatic conditions. However, there are other heavy metal fluxes such as heavy metal input through atmospheric deposition or application of fertiliser, pesticide, manure etc. With regard to predict time to reach the remediation goals and to estimate the costs the heavy metal balances have to consider all the fluxes including their uncertainties.

The objective of this contribution is to determine the parameters required to plan the success of remediation by metal-accumulating plants.

Material and Methods: As a test region we chose the heavy metal contaminated area of Dornach, Switzerland, located approximately 10 km south of Basle. The soil contamination originates from a metal smelter emitting aerosols containing copper, zinc and cadmium during several decades. The area of the contaminated zone is about 4–5 km^2 and comprises mainly agricultural land and residential areas. Estimating average heavy metal balances for a reference area of about 18 km^2 of agricultural land we found that the heavy metal inputs exceeded the removal by plant uptake with crops (von Steiger et.al., 1997).

To test phyto-remediation procedures field experiments were started in April 1997 (reference trial) and will continue until 1999 (treatments techniques to enhance metal uptake by plants). At an agricultural field of 20x30 m, located in the contamination zone of Dornach, metal-accumulating plant species are cultivated, e.g. Brassica juncea, Nicotiana tabacum, Salix viminalis. Each species grow on 3x3 m sub-plots with four randomised replicates in the field. Soil samples were taken down to a depth of 20 cm according to an unbalanced nested sampling design based on a regular grid. The spatial variation of the soil variables investigated was analysed by calculating the experimental semivariances and by hierarchical analysis of variance (Webster and Oliver, 1990). The copper-, zinc- and cadmium content in soil were determined, in each case the soluble fraction ($NaNO_3$-extract), the total fraction (HNO_3-extract) and as a measure for the bioavailable fraction the EDTA-extract.

Results: The mean and coefficient of variation (C.V.) of the contaminants in soil and plants (reference trial without treatments) and the soil parameters are given in Table 1. The range of the bioavailable fraction related to the total fraction was about 75% for copper, 31% for zinc and 40% for cadmium. The soluble metal contents were less than 1% of the total metal fraction in each case.

Table 1: Mean and coefficient of variation of heavy metal content in soil and plant and soil parameters

soil	n = 48	**mean**	**C.V.[%]**		**mean**	**C.V.[%]**
Cu	HNO_3 [ppm]	525	10.3	**CEC** [meq/100g]	30.9	11.8
	EDTA [ppm]	402	12.6	**pH**	7.6	0.7
	$NaNO_3$ [ppm]	0.8	24.7	**org. matter** [%]	5.2	10.9
Zn	HNO_3 [ppm]	697	11.3	**clay** [%]	31.9	13.1
	EDTA [ppm]	214	19.7	**$CaCO_3$** [%]	10.9	24
	$NaNO_3$ [ppm]	0.09	38.1			
Cd	HNO_3 [ppm]	2.7	10.4			
	EDTA [ppm]	1.1	15.5			
	$NaNO_3$ [ppm]	0.001	22.5			
plant	Brassica juncea	(n=16)		Nicotiana tabacum	(n=16)	
Cu	ppm	21.4	18		37.9	15
Zn	ppm	129	16		146	14
Cd	ppm	1.06	15		3.4	24

For copper and zinc the bioavailable content correlated well with the total content. Large correlations were also found between these metals. With regression analysis the soil parameters dominating the distribution of metals between soluble or bioavailable metal fractions and total metal fraction were identified. The pH value, CEC, and in some cases, organic matter and clay content were found to control the soluble or bioavailable fraction. Most of the soil parameters and the HNO_3 and EDTA extractions showed a spatial auto-correlation within the range of about 6-9 m. The soluble metal contents and CEC showed an autocorrelation structure within 1 m.

The heavy metal content in plants refer to a reference uptake. In 1998 different heavy metal mobilisation techniques will be applied in order to enhance the plant metal uptake. Pot experiments under controlled mobilisation conditions showed an plant uptake enhancement factor of about 10 for zinc and of about 20-30 for cadmium (Wenger and Gupta, 1997). The results are used to calculate the estimation error within and between the 3x3 m sub-plots of different metal-accumulating plants.

Conclusions: The relation between the heavy metal contents of plants and the soil parameters dominating the bioavailability of metals in soil will be used to predict the heavy metal extraction from contaminated soil. On this basis we can choose the parameters required for remediation planning and uncertainty quantification of heavy metal extraction.

References:

von Steiger B., Keller A. and Schulin R.(1997) Regional mass flux balancing for controlling gentle soil remediation operations; in: Nutrient Cycling in Agro-ecosystems, ISSS Workshop Soil and Water Quality at Different Scales, Wageningen, Netherlands

Webster R. and Oliver M. A.(1990) Statistical Methods in Soil and Land Resource Survey, Oxford, Oxford University Press

Wenger K. and Gupta S. (1997) Kann eine kontrollierte Mobilisierung die Phytoextraktion von Schwermetallen wesentlich erhöhen? in: Bodenkundliche Gesellschaft Schweiz Bulletin 21, p.91-96

INTEGRATED LONG-TERM MANAGEMENT OF RADIOACTIVELY CONTAMINATED LAND: THE CESER PROJECT

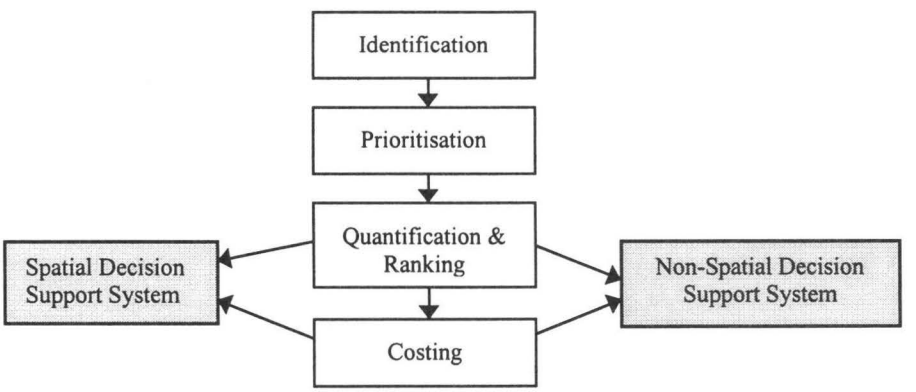
C.A. Salt[1] and S. Rekolainen[2]
[1] Dept of Environmental Science, University of Stirling, Stirling, FK9 4LA, UK
[2] Finnish Environment Institute, Impact Research Division, P.O. Box 140, 00251 Helsinki, Finland

Keywords: radioactive contamination, environmental management, cost-benefit analysis, models, mapping.

The work presented is part of an EU funded project under the Nuclear Fission Safety Programme entitled: Countermeasures: Environmental and Socio-Economic Responses (CESER) and involves partners in Austria, Finland, Germany, Norway and the UK.

Accidents at nuclear installations can cause widespread long-term contamination of soils. On land used for agriculture this necessitates countermeasures to reduce the transfer of radionuclides into the human food chain. A wide range of countermeasures have been evaluated in European countries in the aftermath of the Chernobyl accident [1]. The main aim of this evaluation has been to identify the most effective and practical techniques for reducing the radiation dose to humans. In comparison, little attention has been paid to the potential long-term impacts of these measures on the functioning of agri-ecosystems and their economic value. It is conceivable that environmental and economic costs due to these impacts may equal or even outweigh the benefits of dose reduction. Thus any changes in the economic and ecological values of resources should be considered by decision-makers as part of a comprehensive remediation strategy.

Countermeasures involve processes such as deep ploughing to bury contamination, soil application of fertilisers that compete with radionuclides in the soil solution, use of binding agents in soils or livestock, changes in livestock management or in land use, e.g. afforestation. These may have significant impacts on the quality of soil, water and air; the health of plants, animals and humans; the quality and quantity of the products; and the diversity of landscapes and organisms. The following approach is being adopted in the CESER project to assess these impacts:



Initially a comprehensive list of potential countermeasures and their impacts was compiled. These were then prioritised for case study areas in Finland and Scotland on the basis of four radioactive deposition scenarios and existing agricultural production

systems. The impacts selected are either quantified through calculations and simulation modelling or qualitatively assessed on the basis of expert knowledge. The models ICECREAM[2], OPUS[3] AND PHREEQC[4] were chosen to simulate environmental changes due to countermeasures. The simulations will provide matrices of erosion, nutrient losses and chemical changes in soil solution for the most common soil types, climates, slopes, land use categories and land management practices within the selected geographic areas. Within a geographical information system (GIS) the model output matrices are linked to spatial data sets covering topography, soil types and land uses. This enables the mapping of impacts for different countermeasures.

Environmental cost-benefit analysis is used to estimate off-site costs such as loss of fisheries or amenity value and benefits such as reduced radiation risk arising from the application of countermeasures. Costs will be derived by combining the environmental modelling results with valuations from the literature. Selected impacts such as landscape changes are being valued through an original 'willingness to pay' survey. The direct monetary costs of countermeasures will be included in the final analysis.

Multicriteria Decision Making (MCDM)[5] has been chosen as the methodology for integrating the assessments of impacts and costs resulting from countermeasures. This methodology will provide the decision-maker with a set of countermeasure suitability rankings or suitability maps based on the quantitative and qualitative impacts.

The MCDM approach will be embedded into two types of decision support system. The first will be a non-spatial assessment for a single area, built as a piece of stand alone software using Visual Basic. "Wizards" will take the user down a series of decision trees regarding the type of agriculture and the deposition scenario. Based on this information the user is presented with a selectable list of countermeasures. Once the user has made the selection he/she is asked to provide additional information on site properties which might limit the application of the countermeasures. The impacts, costs and benefits of the countermeasures are then assessed qualitatively and quantitatively using the MCDM methodology.

The second system will be a more generic suitability assessment of a larger, heterogeneous area using a GIS. A suitability assessment will be performed using spatial data within the GIS. Thematic maps depicting site suitability for a single countermeasure or showing the overall "most suitable" countermeasure can be created. By being custom built for this project, both Decision Support Systems should prove to provide greater flexibility, specificity and user-friendliness compared to commercially available software packages.

---

[1]IAEA (1994). *Guidelines for Agricultural Countermeasures Following an Accidental Release of Radionuclides*. Technical Report Series No.363. IAEA, Vienna.

[2] Rekolainen, S. & Posch, M. (1993). Adapting the CREAMS model for Finnish conditions. *Nordic Hydrology*, 24, 309-322.

[3] Smith, R. E.(1992). *OPUS, An Integrated Simulation Model for Transport of Non-point-Source Pollutants at the Field Scale*. U.S. Department of Agriculture, Agricultural Research Service, ARS-98; Fort Collins.

[4] Parkhurst, D.L. (1995). *User's Guide to PHREEQC - a Computer Program for Speciation, Reaction-Path, Advective-Transport and Inverse Geochemical Calculations*. U.S. Geological Survey, Water-Resources Investigations Report 95-4227.

[5] Voogd, H. (1983). *Multicriteria Evaluation for Urban and Regional Planning*. London Pion.

STABILISATION OF HIGHLY POLLUTED SOILS

A. Kontopoulos, P. Theodoratos

Department of Mining and Metallurgical Engineering
National Technical University of Athens
GR-157 80 Zografos, Athens, Greece

Key words: stabilisation, remediation, biological tests, heavy metal, lead, toxicity decontamination.

In situ application of stabilisation techniques may be an economically and environmentally viable solution to the severe problem of heavy metal contaminated lands. The efficiency of these techniques have been tested for the rehabilitation of the highly contaminated soils around the redundant lead-silver mine of Lavrion (southern Attika, Greece). Improper waste management practiced in this site in the past, has resulted in intensive, in terms of concentration and extensive, in spatial terms, contamination of land with heavy metals (Pb, Zn, Cd, As).

The specific soil sample treated in this study originates from an area which has been used in the past for the deposition of beneficiation tailings. This site is actually a residential area and extensive parts are used for home-growing crops, mainly vineyards and olive trees. The soils are hazardous because of (a) the elevated concentration of heavy metals (Pb=2.48%, Zn =2.02%, Cd=0.02 %, As 0.2%), b) the high bioavailable-phytotoxic fraction (more than 30% for Pb, Zn and Cd) as estimated with standard soil extracting procedures and c) the fact that they are characterised as toxic according to the EPA-TCLP test (U.S. EPA, 1986).

A number of inorganic and organic waste or low-cost materials was used as stabilising agents, including: Phosphates, fly ash, bentonite, cement kiln dust, biological sludge, compost, saw dust. The most successful experiments were those using phosphates, fly ash and biological sludge. Stabilisation of the soil was done in pot experiments. A quantity of soil, ranging between 600-800 g was mixed with the calculated dose of stabilising agent and placed in a 1 litre pot. The effect of the various additives on the stabilisation of the heavy metals in the soil was evaluated by chemical extraction tests and verified by actual biological tests. Chemical extraction tests included a) the EPA-TCLP test for toxicity characterisation and b) the application of several leaching solutions (EDTA, DTPA and $NaHCO_3$) for the determination of bioavailable-phytotoxic fraction (Page *et al.*, 1982). The biological tests involved plant growth tests using as plant indicator dwarf beans (*Phaseolus vulgaris starazagorski*).

In Figure 1 the effect of additives on the toxicity of the soil as determined by the EPA TCLP Test is given. It is seen that all additives have a pronounced effect in lowering the toxicity of Pb and Cd to below regulatory limits (5 mg/l for Pb and 1 mg/l for Cd). The toxicity of Zn is also drastically reduced with fly ash and biological sludge, but only slightly with phosphates. On the contrary, all additives result in an increase in As leachability, phosphates having the most pronounced effect; nevertheless, in any case As toxicity remains below the 5 mg/l regulatory limit.

Contaminated Soil '98, Thomas Telford, London, 1998, 1115–1116

The evaluation of phytoavailability applying the other leaching tests has led to similar conclusions. Less than 1% phosphate addition reduces Pb "phytoavailability" by 50% and Cd by 40%. Biological sludge and fly ash additions of 10-15% also result in a pronounced decrease in Cd extractability, and to a lesser degree, of Pb and Zn extractability. On the contrary, they increase the extractability of As.

The biological tests were applied in order to evaluate the effect of the stabilising agents on the growth of plants and on the phytoaccumulation of heavy metals. Biological sludge addition was found to have a positive effect on the production of biomass, while phosphates and fly ash show a negative effect. The analyses of plant tissues (leaves and roots) have shown that the addition of stabilising reagents was not particularly efficient in reducing the uptake of metals by the plants.

Based on the above conclusions, the following rehabilitation method is proposed for further testing under field conditions: treatment of the soil with an appropriate and cost-effective mixture of the stabilisers tested in order to immobilise the heavy metals and promote the production of phytomass, followed by the application of a decorative self sustained vegetation, aiming at suppressing wind erosion.

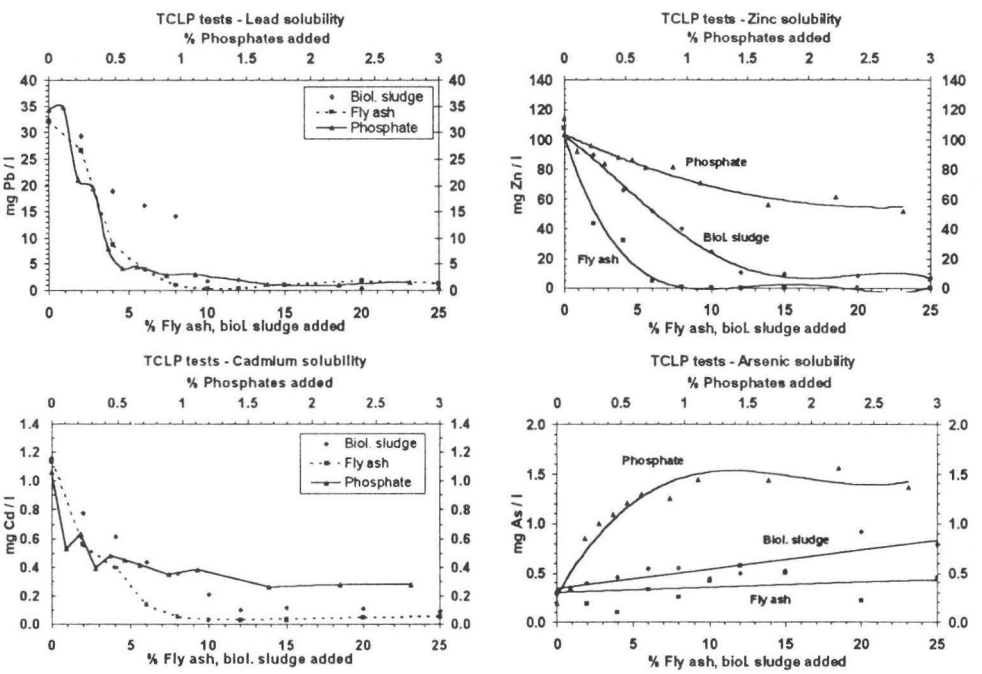


Fig. 1: Effect of additives on Pb (a), Zn (b), Cd (c) and As (d) Toxicity in soil. Leachate concentration (in mg/l) vs. stabilizer added

REFERENCES

U.S. EPA (1986) Toxicity characteristic leaching procedure, Appendix 1, Federal Register 51:216.

Page, A.L.,. Miller, R.H and Keeney, D.R (1982) *Methods of soil analysis,* AGRONOMY Series No 9, part 2, Madiso, Wiscosin USA.

THE FEASIBILITY OF *IN SITU* BIOREMEDIATION OF GROUNDWATER NITRATE

Dr. Elise Cartmell[a], Prof. Lewis Clark[a], Mr. David Oakes[a], Dr. Stephen Smith[a] and Prof. Howard Wheater[b].
[a] WRc plc, Henley Road, Medmenham, Marlow, Bucks, SL7 2HD.
[b] Department of Civil Engineering, Imperial College of Science Technology and Medicine, Imperial College Road, London, SW7 2BU.

Key Words: nitrate; *in situ* bioremediation; groundwater; microcosms.

SUMMARY
In situ bioremediation of high nitrate groundwater may provide significant advantages over conventional treatment processes. Technology may be simpler to operate with reduced costs and utilise sustainable treatment methods which do not generate a waste stream. This work programme, funded by the Environment Agency and Severn Trent Water, utilises a biochemical transport model (developed from a model by the University of Heidelberg, Germany) to minimise the costs of evaluating different strategies for *in situ* bioremediation for denitrification and provide a quantitative basis of optimising system design and configuration. Ongoing laboratory experiments assess the potential for aquifer biofouling and optimum substrate injection regimes and concentration.

BACKGROUND
Thirty per cent of potable water supplies are abstracted from groundwater in the UK, and blending or nitrate removal is practised in a number of areas to comply with drinking water quality standards. The cost of conventional treatment processes is high and alternative, novel, sustainable solutions need to be sought.

Biological denitrification is the process of nitrate reduction by microorganisms to gaseous forms of nitrogen. This process occurs naturally in groundwater systems when the supply of organic carbon substrate is adequate to sustain denitrification activity. It potentially can be harnessed, through the external supply of organic carbon, to provide a sustainable method of groundwater treatment by *in situ* aquifer bioremediation.

WRc and Imperial College have modelled denitrification in groundwater systems using a biochemical reactive transport approach. Model parameterisation was based on data obtained from a laboratory microcosm flow-through apparatus using Triassic sandstone material. The results have clearly outlined the potential for natural biological denitrification as a process for removing nitrates from groundwater.

Contaminated Soil '98, Thomas Telford, London, 1998, 1117–1118

METHODOLOGY

The modelling approach is now being used to assess the feasibility of *in situ* bioremediation of nitrate in a sandstone aquifer, and to evaluate optimum remediation design schemes.

Laboratory studies are also underway to continue the parameterisation of the biochemical model particularly in relation aquifer biofouling potential using the developed flow-through microcosm apparatus. Overall experimental objectives are:

- Determination of the potential for biofouling of substrate-injection borehole facilities and surrounding aquifer material. The significance and extent of biofouling is measured by correlating potential decreases in permeability and porosity of the sandstone media with carbon input, flow rate and microbial biomass ATP concentrations.
- Determination of the commencement of denitrification under aerobic aquifer conditions using excess carbon to generate denitrification conditions. Further optimisation of the minimum carbon concentration required can be found through application of the current denitrification model.
- Determination if re-circulation of nutrient solution by injection boreholes enhances nitrate removal and / or improves water quality.
- Assessment with regard to mode of operation of substrates e.g. continuous or plug-flow.
- Determination of the quality of the treated water in relation to residual organics, nitrite, oxygen concentrations or bacterial contamination.

CONCLUSIONS

There are various possible configurations of treatment system for *in situ* bioremediation involving injection and abstraction boreholes for carbon and biological management. However, optimising the design specification is a critical step in achieving effective operation to avoid biofouling and abstracted water contamination by residual organics and bacteria. This requires a thorough understanding of the biochemical processes and hydrology within the aquifer system. The opportunity to simulate *in situ* bioremediation and to test the feasibility and cost-effectiveness of this approach compared to conventional surface treatment can be achieved through the application of the denitrification model and laboratory bioremediation optimisation.

Phytoremediation Of Heavy Metal Contaminated Sites By Potential Fibre Crops

John Kerr, Ian Pulford, Harry Duncan, Chris Wheeler
University Of Glasgow
Environmental Chemistry, University of Glasgow, Glasgow, G12 8QQ
Key words: bioremediation, contaminated soil, heavy metals, plants

Introduction

Our industrial past has left us with a legacy of contaminate land much of which is polluted by heavy metals, but have new problems to cope with in addition. Chief amongst these is the ban on sewage dumping at sea. Sewage sludge often has a high heavy metal content, both from industrial and domestic sources. Thus metal contamination in soil looks set to be a problem of the foreseeable future.

This study will look at crops which have a potential to make a financial contribution to the remediation of the site on which they are planted. The particular area of study will be plants which may be suitable for the paper and fibre industry.

The plants under study are elephant grass (*Miscanthus giganteus*), stinging nettles *Urtica dioica* and flax/linseed (*Linum usitatissimum*) . All of these carry the potential to act as feed stocks for the paper and fibre industry.

Experimental set-up

A pot experiment was designed to assess the ability of the crops to tolerate high levels of metal contamination, and establish their ability to extract contaminating metal ions from the spoil. The spoils used were artificially created by mixing a good quality brown earth soil with a coarse gravel and the chloride salts of the metals in the study. Control spoils were made up in the same way but with the metal salts absent. The spoil treatments were zinc 500 ppm, zinc 3000 ppm, copper 500 ppm, copper 2000 ppm, nickel 500 ppm, nickel 1000 ppm, cadmium 300 ppm, cadmium 1000 ppm and lead 2000 ppm. There was also a soil treated with sewage sludge annually for over fifty years included in the study. The sewage sludge soil has high levels of all the metals. The following metal concentrations were found in the sewage sludge soil: zinc 2000 ppm; copper and nickel 850 ppm; chromium 2000; cadmium 40ppm and the lead was 700 ppm

Results and Discussion

The high levels of zinc, copper, nickel, and cadmium were too phytotoxic for the plants, which either failed to produce shoots or started to grow but subsequently died, though one miscanthus plant did survive the high nickel treatment. Yield data are detailed in table 1. Miscanthus growth was good for both the low zinc and the lead treatments but was poor for the other metals. The sewage sludge treatment also gave a low yield for miscanthus,contrasting with the other two species. The flax yield was poor or zero in five of the metal treatments with good growth only in the lead and sewage sludge treatments. The nettle yields were good in the copper, chromium and lead treated soils. The other metals gave a poor yield and there was no growth in nickel treated soil. The growth of nettles in the sewage sludge treated soil was however very good indeed, likely due to the high fertility.

Assessing the ability of the plants to extract the contaminating metals from the spoils was the main objective of the study. Metal concentrations in the plant tissues are detailed in table 2. Though the growth was poor in many of the metals, Miscanthus growing in the 500 ppm zinc soil gave both a good yield and a high metal uptake. The

zinc concentrations of the plant tissues were almost double the spoil concentrations, hence there was a concentration effect. Nettles also showed a significant concentration of cadmium in their tissue but coupled with a low yield this result is not as promising.

Table 1

	Plant Yields Expressed as a percentage of the growth of the control treatment.		
Soil Treatment/Plant	Miscanthus	Flax	Nettle
Control	59.65 (g)	51.85(g)	9.99 (g)
	(%)	(%)	(%)
500 (ppm) Zinc	72	3	34
500 (ppm) Copper	10	NG	63
500 (ppm) Nickel	0.3	NG	NG
1000 (ppm) Nickel	2	NG	NG
300 (ppm) Cadmium	6	NG	10.43
2000 (ppm) Chromium	0.4	0.5	50
2000 (ppm) Lead	92	69	84
Sewage Sludge	26	66	386
NG: no growth			

Table 2

	Average Metal Concentration Of Plant Tissue					
	Plant Tissue		Plant Tissue		Plant Tissue	
Soil Treatment	Miscanthus	(ppm)	Flax	(ppm)	Nettle	(ppm)
500 Zinc	Stems	969	Roots	NG	Stems	171
	Leaves	868	Stem & Leaf	NG	Leaves	192
500 Copper	Stems	7	Roots	176	Stems	4
	Leaves	10	Stem & Leaf	19	Leaves	11
500 Nickel	Stem & Leaf	186	Roots	NG	Stems	NG
			Stem & Leaf	NG	Leaves	NG
300 Cadmium	Leaves	176	Roots	NG	Stems	919
	Stems	15	Stem & Leaf	NG	Leaves	852
2000 Chromium	Stem & Leaf	55	Roots	NG	Stems	8
			Stem & Leaf	NG	Leaves	17
2000 Lead	Leaves	119	Roots	417	Stems	194
	Stems	52	Stem & Leaf	33	Leaves	111
NG: no growth						

The levels of metal in the plant tissues for the sewage sludge treatment were all low despite the comparatively high yields. This is most probably due to the high organic matter content of the soil. The difference in the two matrices has given starkly contrasting results in the study with the notable exception of lead. The low organic/high metal matrix of the artificial spoils has led to either plant uptake of the metals (as in the 500 ppm zinc soil) or plant death., whereas the organic rich/high metal matrix of the sewage sludge has led to good growth but little metal uptake.

Conclusions

The study has shown that of the three crops considered all grew well in the sewage sludge soil despite its high concentrations of phytotoxic metals, and also in the lead soil but in neither case could their metal uptake be considered as phytoremediation of the contaminated material. In the artificial spoils, however, the miscanthus grass did show significant concentration of zinc at 500 ppm. For the other metals and the other crops the metal concentrations proved to be too phytotoxic for the crops survive.

Acknowledgements

We gratefully acknowledge the funding of this research by Scottish Enterprise Network.

A COMPREHENSIVE EVALUATION ON THE USE OF OXYGEN RELEASE COMPOUND IN BIOREMEDIATION

Stephen S. Koenigsberg
Regenesis Bioremediation Products
27130A Paseo Espada, Suite 1407
San Juan Capistrano, CA 92675

Key Words: aquifer, bacteria, barriers, BTEX, chlorinated hydrocarbons, groundwater remediation, in-situ bioremediation, natural attenuation, petroleum hydrocarbons

Oxygen Release Compound (ORC®) is a controlled release oxygen delivery technology being employed on over 3,000 sites worldwide to enhance the natural bioattenuation of contaminated groundwater. ORC is a patented formulation of time-release magnesium peroxide (Koenigsberg and Farone, 1993), developed by Regenesis Bioremediation Products. The rate control feature of ORC is a function of the synthesis of the molecular matrix and not achieved by a coating process. This specialized form of magnesium peroxide and its residue, magnesium hydroxide, are insoluble and non-toxic; oxygen is simply released during hydration by the following reaction (1):

$$MgO_2 + H_2O \rightarrow 1/2\ O_2 + Mg(OH)_2 \quad (1)$$

The molecular oxygen is then available for the biological remediation of a wide range of aerobically degradable compounds such as TPH, BTEX, MTBE, and VC. Since there are already natural, oxygen limited processes that drive the degradation of these compounds, ORC represents a viable method of *enhancing* the natural rate of attenuation and *reducing* the time to site closure.

An ORC treatment represents a "low intensity" approach to site remediation - providing a simple, passive and low-cost method of stimulating bioremediation. In many cases, alternatives such as air sparging and pump and treat are more capital and management intensive, while failing to deliver any significant advantages. Several specific examples of ORC use and efficacy will be reviewed in this paper.

ORC can be packaged in exchangeable filter socks and contacted with contaminated groundwater via an array of wells or trenches to form an "oxygen barrier" to contaminant flux. ORC powder can be made into a slurry that is backfilled or injected into the saturated zone; or, it can be dispersed as dry powder into contaminated soil in order to attack the source. Applications of ORC, by socks, slurry or powder, provide oxygen at a timed rate that is generally consistent with demand. This allows sites to be passively managed in contrast to the actively managed alternatives discussed.

The enhancement of natural attenuation is centered around the principle that any significant reduction of contaminant mass will facilitate the shrinkage of the contaminant plume. Pulling the edge of the plume (the "zero-line") back towards the source is an integral part of risk-reduction program standards. On many sites, in order to achieve this, a broad source area can be treated with an array of low cost push point injections. Typically an ORC treatment will cost $25,000 to $50,000 in contrast to alternatives costing several multiples of this.

As just one example, one of the most intensively studied source treatment applications using an ORC slurry was carried out in Great Bend, Kansas. The site had releases from

two gas stations on adjacent corners that formed a commingled dissolved phase hydrocarbon plume over an area 500' x 350'. Although initial investigations and testing revealed that an air sparging and SVE system could be installed, there were several drawbacks. In addition to a capital cost of $300,000, there were both physical limitations for the placement of equipment and residential nuisance issues.

The saturated zone, which consisted of medium to coarse grained sand at eight feet bgs, was treated with ORC placed by push point injection. Groundwater was flowing east at a rate of about 0.2 ft/day. Based on calculations of BTEX mass in the core of the plume, 2,325 pounds of ORC were injected into 118 points throughout the site. After seven months, BTEX was reduced 69%, benzene was reduced 48%, and GRO was reduced 60%. The cost of this project was $23,600 for ORC plus an equal amount of money spent on implementation - a substantial savings over alternative treatment methods.

Citing another case, ORC was installed at a service station site in Vancouver, Washington. The treatment zone was approximately 30,800 sq. ft., containing 33 pounds of BTEX. Groundwater flowed to the west at 1-10 ft/day in a shallow, thin aquifer. Fifteen borings about 8 inches in diameter were installed upgradient of the area to be treated and backfilled with ORC. In the first five months levels in the anaerobic core of the plume decreased 64% for total BTEX, 87% for benzene and 74% for GRO. The 15 borings were each filled with approximately 65 pounds of ORC at a total cost of about $10,000. With other capital and operating expenses the total application cost was $40,000 - a significant savings over the estimated $250,000 to implement more active remedial technologies. Closure is expected on the site in 18 to 36 months.

There is recent evidence that ORC can be used in to remediate the gasoline oxygenate, methyl tertiary butyl ether (MTBE). MTBE is a ubiquitous compound that seriously complicates the remediation and closure of properties contaminated with fuel hydrocarbons, primarily because it degrades very slowly under aerobic conditions. The literature first reported that aerobic degradation of MTBE is possible; we now know that 1) the rate of MTBE degradation is a function of oxygen concentration and that 2) removal of BTEX facilitates the degradation of MTBE. Both of these factors can be positively affected by ORC. New data from six sites utilizing ORC treatment technologies, varying from slurry injections to oxygen barriers, shows an average MTBE reduction of 81% following six months of treatment. Laboratory experiments have shown that ORC does not react directly with nor volatilize MTBE; therefore, bioremediation is the presumptive mechanism of removal.

The use of ORC for the enhanced bioremediation of dichloroethene (DCE) and vinyl chloride (VC) is currently being studied. The presence of oxygen has been shown to stimulate both the aerobic degradation and co-metabolism of DCE and VC and is the basis upon which ORC has been shown to effectively enhance remediation of these contaminants. The enhanced bioremediation of DCE and VC using ORC is currently being demonstrated at an industrial site in which ABB Environmental Services is conducting a dual phase treatment of a contaminant plume containing chlorinated hydrocarbons. The first phase of treatment is the enhanced anaerobic biodegradation of the higher order chlorinated compounds (PCE and TCE) through the addition of organic acids. The daughter products of the first phase of remediation, DCE and VC, are being treated in the second phase through the addition of ORC to the system. Monitoring data indicate that ORC has truncated and reversed the rise in DCE and VC resulting from the first phase of treatment.

DECONTAMINATION OF MERCURY POLLUTED SOILS BY ELECTROLEACHING: ASSESSMENT OF THE ECOLOGICAL CLEAN-UP BENEFIT

J. Thöming[1], S. Franke[2]

[1] Technical University of Hamburg-Harburg, Dept. of Environmental Technology Eissendorfer Str. 40, D 21073 Hamburg e-mail: thoeming@tu-harburg.d400.de
[2] University of Hamburg, Institute of Organic Chemistry, Martin-Luther-King-Platz 6, D 20146 Hamburg, Germany

Key words: availability, biotoxicity, chlorinated hydrocarbons, electrolysis, extraction, heavy metals, leaching behaviour, mercury, oxidation, physico-chemical processing

INTRODUCTION

Dealing with heavy metal contaminated soils a particular attention is given to mercury because of its special physico-chemical properties and the high toxicity of some of its species, especially the methyl mercury. Excavated soil containing mercury has to be long-term deposited at great expense or it has to be decontaminated usually by retorting processes. Electroleaching offers a cheaper alternative which is a hydrometallurgical process combining wet extraction and electrolytical preparation of the leachate (Figure 1). There are two advantages of such a process compared with retorting processes. Because of far larger thermodynamic separation factors the capital costs are much lower. Moreover, air pollution problems are avoided [1].

During electrolysis the redox potential of the chloride solution increases dramatically. Consequently this solution is capable to oxidise Hg(0) and Hg(I) compounds in soils readily to Hg(II) and to extract this species forming strong and soluble tetrachloromercurate complexes. The mercury loaded aqueous stream is treated again electrolytically: mercury is deposited cathodically and reagent is regenerated.

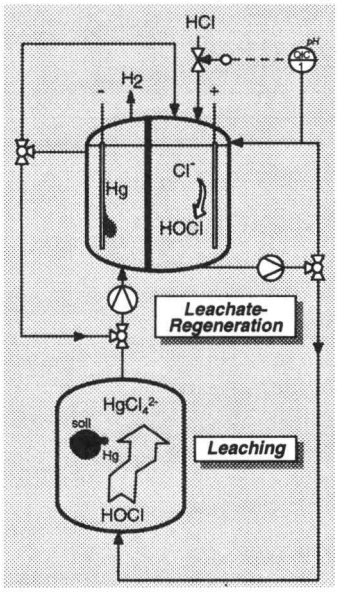


Fig. 1 Electroleaching process: leaching and electrolysis for recovery of mercury as well as in-line production of leaching agent

RESULTS AND DISCUSSION

To assess the performance of the decontamination three parameters have been investigated treating three different soils: (1.) total mercury content, (2.) toxicity (photobacterium phosphoreum) of the soil and (3.) chlorinated byproducts. It can be shown that the mercury reduction rate increases with increasing initial mercury concentration. The total mercury content could be lowered beneath the German LAGA-value [2]. Nevertheless the toxicity behaves different: It does not correlate neither with

content of mercury nor with content of organic matter (loss of ignition) as can be seen in Figure 2.

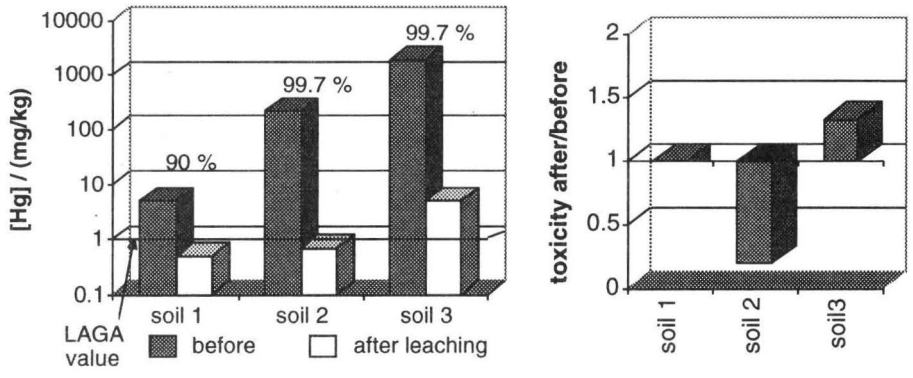


Fig. 2 a) Mercury reduction rate in % and residual concentrations compared with LAGA-value; b) change in toxicity before and after treatment

In soil 2 a total of 25 chlorinated compounds was detected by GC/MS analyses. Out of these the 14 compounds given in Table 1 were identified, the assignment of tetrachlorocyclopropene being tentative. After leaching the amount of chlorocompounds in the soil generally is reduced relative to the original content, but single compounds (e.g. hexachlorobenzene) may behave differently.

The pH-dependence of the relative amounts of chlorinated compounds indicates that a production of by-products formed due to chlorination of organics can be avoided selecting optimized leaching parameters. Comprising these results the ecological benefit of a clean-up by electroleaching can not be assessed easily. Further optimizations of the process with regard to a minimization of toxicity are needed.

Tab. 1 Relative amounts of selected chlorinated compounds in contaminated soil leached at pH5 and pH 6

	rel. amount	
Compound Leaching at	pH 5	pH 6
Tetrachlorocyclopropene (?)	<0.1	0.5
Trichloroacrylic acid methyl ester	0.5	1.2
Hexachloroethane	0.2	1
Tetrachlorobutadiene Isomer 1	<0.1	<0.1
Tetrachlorobutadiene Isomer 2	<0.1	<0.1
Tetrachlorobutadiene Isomer 3	<0.1	<0.1
Tetrachlorobutadiene Isomer 4	<0.1	<0.1
Pentachlorobutadiene Isomer 1	<0.1	0.2
Pentachlorobutadiene Isomer 2	0.1	0.4
Pentachlorobutadiene Isomer 3	<0.1	0.1
Hexachlorobutadiene	0.1	0.5
Tetrachlorobenzene	<0.1	<0.1
Pentachlorobenzene	0.1	0.3
Hexachlorobenzene	1.7	0.9

REFERENCES

[1] Hempel, M., Thöming, J. (1997) Remediation techniques for Hg-contaminated sites with emphasis on Europe. In: Ebinghaus, Turner, Lacerda, Vasiliev & Salomons, Mercury Contaminated Sites. Characterization, Risk-Assessment and Remediation. Springer Environmental Science

[2] LAGA (1995) Anforderungen an die stoffliche Verwertung von mineralischen Reststoffen / Abfällen (Technische Regeln). Länderarbeitsgemeinschaft Abfall. In: Rosenkranz D, Einsele G, Harreß G (Hrsg.) Bodenschutz, 2. Bd., Erich Schmidt Verlag, Berlin

TREATMENT OF HYDROCARBON CONTAMINATED GROUNDWATER BASED ON HYDROLOGICAL TESTS

P. Szabó, G. Nagy

MEGATERRA LTD, 1126 Budapest, Zulejka u. 4. HUNGARY

Hydrocarbon contaminated groundwater is a common environmental problem in Hungary. Leakage of underground storage tanks, pipe break or illegal tapping as well as lorry accidents can be mentioned as main reasons.
MEGATERRA LTD elaborated, adopted and tested several groundwater clean-up methods. These methods are based on detailed survey and investigation, sampling and analysis, delineation of contaminated groundwater, risk assessment, establishment of monitoring wells, pumping tests and remediation action plan.
An automatic system was designed and implemented to provide suitable depression. Installation and operation of different extraction technologies using extraction wells with pumps, vacuum wells (Figure 1.) and extraction drainage system (Figure 2.) were deeply studied and compared.

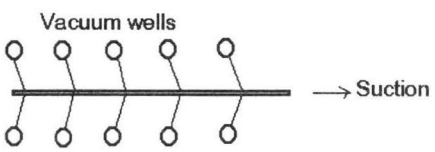
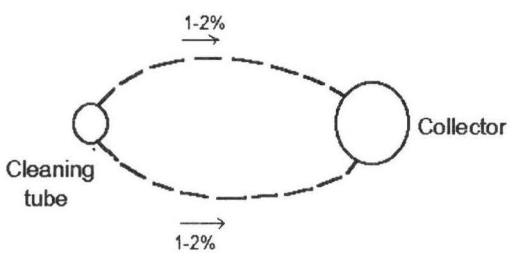


Figure 1.



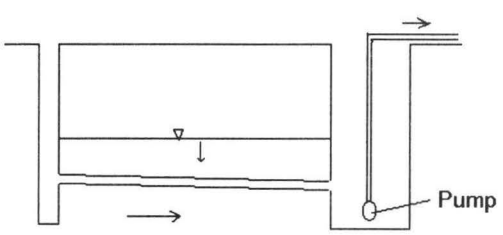


Figure 2.

During the on-site work removal methods of free CH phase with separation pumps, skimming and adsorbents were selected according to the site properties.

Contaminated Soil '98, Thomas Telford, London, 1998, 1125–1126

MEGATERRA LTD developed a system to clean up groundwater contaminated by soluble hydrocarbons. Different adsorbing materials including types of active coal, clay minerals and fibre by-products were tested and compared.
Quality control of and data from the monitoring wells can prove the efficiency of our groundwater treatment methods (Table 1.)

Project	TPH mg/l inlet water	TPH mg/l outlet water
"Debrecen"	16,80-17,50	0,56-0,61
"Budapest"	0,85-1,24	0,10-0,15

Table 1.

Flow diagram of the treatment process is shown on Figure 3.

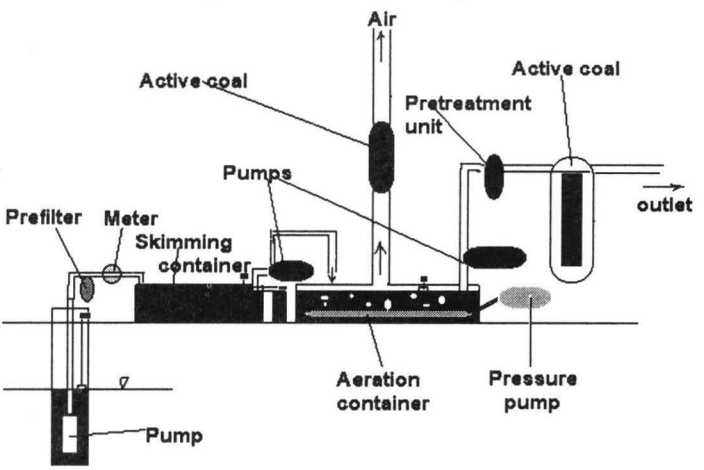


Figure 3.

References:

Barótfi, I. (1990): *Környezettechnika Kézikönyv*, Környezettechnikai Szolgáltató Kft, Budapest

Exner, J. H. (1982): *Detoxication of Hazardous Waste*, Ann Arbor Science, Collingwood, Michigan, USA

Förstner, U. (1993): *Környezetvédelmi technika,* Springer Hungarica Kiadó Kft. Budapest

Ground-Water Treatment technology Resource Guide, EPA (1994), Washington, USA

Olessák, D. (1995): *A talajtisztítás és ipari gyakorlata*, Környezetgazdálkodási Intézet, Budapest

Papp, S. - Kümmel, R. (1992): *Környezeti kémia*, Tankönyvkiadó, Budapest

The Superfund Innovative Technology Evaluation Program: Technology Profiles, Fifth edition, EPA (1992), Washington, USA

Vilma J.F. Visser (1993): *Contaminated Land Policies In Some Industrialized Countries*, Technical Soil Protection Committee, The Hague, The Netherlands

A MODEL PROCEDURE FOR EVALUATION AND SELECTION OF REMEDIAL MEASURES FOR CONTAMINATED LAND

M V Smith, Stanger Science and Environment, Roadstone House, 50 Waterloo Road, Wolverhampton WV1 4RU, UK

Key words: Governmental, models, remediation, risk management.

A model procedure for the evaluation and selection of remedial measures has been developed as part of the Environment Agency's contaminated land research programme. The procedure is one of a series of model procedures being developed by the UK Department of the Environment, Transport and Regions and the Environment Agency, which address the whole process of assessing and managing risks that may be associated with contaminated land *(Herbert et al, 1995)*. The procedures aim to provide structured framework which integrates current good practice and guidance for dealing with contaminated land in a risk-based context.

Model procedures are being developed to cover the main activities involved in assessing and managing risks from contamination namely:

i) Model Procedure for Risk Assessment.

ii) Model Procedure for Evaluation and Selection of Remedial Measures.

iii) Model Procedure for Implementation of Risk Management Actions.

The Model Procedure for Evaluation and Selection of Remedial Measures for Contaminated Land has been developed to be applicable to individual sites and where action is required to deal with risks affecting the current use, or where re-development is planned. In many instances the Procedure will be used after completion of the Model Procedure for Risk Assessment, which is described in more detail in another paper in this conference *[paper by M R Harris to Theme B of the Conference]*. However, the Procedure is also applicable in circumstances where decisions need to be made on appropriate remedial action following identification of a situation requiring emergency action, in response to regulatory intervention or in circumstances where demands of corporate policy may dictate remedial action.

The aim of the model procedure is to assist users to select a remedial strategy which is technically suitable for the risk characteristics and environmental setting of the site, able to meet the required targets or objectives for the remedial action, cost-effective and suitable for the actual or intended use of the site. This requires that technical and non-technical factors are evaluated and an appropriate balance achieved for the particular circumstances. The procedure sets out a clear and structured approach to this process, and aims to encourage rational and defensible decisions about the most appropriate remedial solution.

Contaminated Soil '98, Thomas Telford, London, 1998, 1127–1128

The Procedure is based on 4 main stages or tasks which need to be undertaken:

i) Review of Available Data: establishing that sufficient information is available about the site and the reasons for remedial action to allow proper evaluation and sensible decisions to be made.
ii) Identification of Potential Remedial Options: evaluating available remedial measures to identify a limited number of options potentially appropriate for treating the site as a whole.
iii) Detailed Analysis of Alternative Options: analysing the advantages and disadvantages of each remedial option, taking into account site specific constraints, using a number of parameters including costs and benefits.
iv) Selection of Preferred Strategy: selecting the preferred strategy by comparison of the extent to which each remedial option analysed under Stage 3 meets the remedial objectives, and the associated level of confidence.

The selection process is based on comparison between different theoretically suitable options taking into account site specific circumstances and the relative costs/benefits of a particular strategy.

Objectives set at the start of the selection process may themselves require review and possibly modification during the process, for example review may be needed where:-

- a suitable remedial strategy can not be identified to meet the initial objectives;
- there are changes in the management context of the site e.g. where external parties become involved (as future investors, tenants, owners etc);
- specific objectives vary, such as timescale.

The opportunity to reference back between the various stages, including the management context, is available as the assessor proceeds through the process. Provision for this iteration is important because it is possible that procedural steps may need to be repeated in the light of better or further information. The final selection should represent a balanced judgement on which of potentially many remedial measures offers the most cost-effective and technically satisfactory solution against the project objectives.

The approach outlined in this paper enables users to introduce individual selection parameters appropriate to their situation. In this way, it is hoped that the procedure can encourage a consistent approach to the process of deciding which form, or forms, of remedial action are most appropriate to deal with the unacceptable risks identified, whatever the circumstance of the site.

ACKNOWLEDGEMENTS

This paper has stemmed from work associated with a Department of Environment, Transport and Regions and Environment Agency research contract. The views expressed in this paper, however, are those of the author and not necessarily those of the DETR/Environment Agency.

REFERENCE

Herbert, S M, Harris M R, Denner J (1995). UK standard procedures for contaminated land. In *Contaminated Soil '95 vanden Brink, W J Bosman, R Arendt, F Kluwer Academic Publishers.*

RECOMMENDATIONS ON QUALITY CRITERIA FOR REMEDIATION OF CONTAMINATED SITES

U-M. Mroueh
VTT Chemical Technology, P.O. Box 1403, FIN-02044 VTT, Finland

Key words: remediation, contaminated sites, treatment, clean-up technologies, guide levels, quality control, practice

A guidance document on the investigation, analysis and remediation of contaminated sites was published as a part of the technology programme "Environmental technology in construction" funded by the Finnish Technology Development Centre, Tekes. The development of remedial technologies for contaminated soil is one of the research areas included in the programme. The document was prepared by two Finnish research institutes, VTT Chemical Technology and the Geological Survey of Finland.

The objective of the document is to assist the parties involved in remediation projects, including owners of contaminated sites, consultants, contractors and regulatory bodies, by giving recommendations on good practice during the various phases of investigation and remediation. The survey is based on expert information and guidance documents collected both from Finland and from those countries which have substantial experience of remedial activities.

The report presents recommendations on quality criteria for the treatment methods already used in Finland, as well as for those new methods that will be used in the near future. The remediation technologies discussed include excavation and disposal, solidification, chemical stabilisation, containment, wet separation, thermal treatment methods, composting and soil vapour extraction. In addition, guidance is presented on the development of remediation strategies, on the management of the entire process and on the quality control during various stages of remediation.

After the remediation targets are set, the applicability of the treatment methods should be confirmed with method- and site-related compliance testing. As an example, test procedures and recommended target values for solidified waste soil are presented in table 1.

Guidance is also given on the quality control and the control methods to be used during the entire project. The quality control system is divided into two parts: the contractors quality control system and an independent control by an outside party. The task of the outside controller is to ensure sufficient and relevant quality control, by inspections, control samples, etc.

Requirements and procedures for high quality documentation during all the process stages are presented as an essential part of the quality control system. The documentation shall be sufficient for the follow-up of the procedures and for the evaluation of all the conclusions made. In the final report the compatibility of the results with the criteria set shall be proven for approval of the remedial actions.

Contaminated Soil '98, Thomas Telford, London, 1998, 1129–1130

Parameter	Recommended test method	On-site disposal	Landfill disposal
Concentration of contaminants		Below lower guide values presented in the document	Below higher guide values presented in the document
Leaching of contaminants	Standard Leaching Test NEN 7345	Leached concentrations below guide values presented in the document	Leached concentrations below guide values presented in the document
Confined compressive strength		$\geq 3{,}5$ MN/m^2	$\geq 1{,}0$ MN/m^2
Water permeability		$\leq 10^{-9}$ m/s	$\leq 10^{-8}$ m/s
Freeze-thaw test			12 cycles, weight loss < 10 %.

Table 1. Recommendations for test methods and for target values for solidified waste soil disposed on-site and for solidified waste soil used in landfills.

Minimisation of environmental impacts is included in the report as a part of a high-quality project. The transfer of contaminants into water, air and clean soil shall be prevented by selection of the most appropriate remedial method or by using effective emission reduction technologies. Recommendations on emission values for thermal treatment technologies and for emissions of volatile compounds, as well as for waste waters, are presented. Precautionary measures for the safety of workers and for the protection of the surroundings are also discussed.

Post-treatment monitoring or control is required, especially if the contaminants are not removed from the soil by the methods used. The duration of the control is dictated by the method used, the remediation level attained and the results of the control tests.

References:

Mroueh, U-M, Järvinen, H-L. and Lehto, O. (1996) *Investigation and remediation of contaminated soils*. Tekes Technology Review 47/1996.

TREATMENT OF CONTAMINATED SOILS DFG - RESEARCH CENTRE SFB 188

R. Stegmann

Department of Waste Management, Technical University of Hamburg-Harburg, Harburger Schloßstr. 37, 21079 Hamburg, Germany

Key words: contaminated soils, chemico-physical processes, biological processes, scientific principles, fundamentals and evaluation criteria

The research centre "Treatment of Contaminated Soils" was established by the Deutsche Forschungsgemeinschaft (DFG) in 1989. It is the aim of the research centre to investigate, develop and optimise decontamination methods. In addition, analytical and measuring techniques shall be perfected, enabling a rapid and comprehensive description of all processes. To achieve this goal, it is necessary to screen the contaminants, to calculate ecotoxicological limits and to quantify the availability of contaminants for microorganisms.

Soil Protection Engineering has developed into an independent scientific discipline, in which the experience and knowledge of various special disciplines can help find solutions and answers to the problems posed by contaminants. Within the research centre, civil engineers, chemists, microbiologists, soil scientists and geologists cooperate to develop this new field of work.

It is the objective to develop mechanical, chemical and thermal process steps to treat highly contaminated soils and extracts from soil treatment. A major task is the subsequent treatment of the mechanically separated highly charged fine particle fraction. In the end an extensive treatment concept will be available enabling not only to completely deconterminate the most different soil types but also to direct the occurring residues and extracting solutions to an effective and cheap recycling or reuse.
Of particular interest is the development of biological processes with regard to enhancing the bioavailability of contaminants. In new approaches to soil treatment extremely thermophilic microorganisms are used, profiting from the fact that the bioavailability of difficultly soluble contaminants is better at high temperatures. The application of complex biotechnical processes makes only sense when the treatment can be effected within an economically justifiable period of time and the remaining contaminant concentrations are in a range allowing the reutilisation of the treated soil material. Emphasis is placed on investigating in how far the microorganisms are able to perform the desired contaminant turnover processes.

Especially for contaminations covering a wide area and reaching into depth a remedial concept often considered is "leave it as it is". However, there is no scientifically founded knowledge of the long-term consequences of this way of proceeding. Investigations into the aspects of extensiveness, long-term behaviour and the possibility of modelling the contaminant retention shall provide insight in this regard.

The different objectives of the research centre, which were described, are closely related to basic research in natural sciences. In the focus of interest are methodical approaches, permanent redevelopment, optimisation and control of analytical methods, sophistication and extension of rapid analytical processes, characterisation of key parameters relevant for

Contaminated Soil '98, Thomas Telford, London, 1998, 1131–1132

remedial action and to a particular extent questions about mobility and binding of contaminants onto the humin matrix of the soil. In addition, the chemical analyses are completed by ecotoxicological investigations and examinations into degradation performance, toxicity and microbial activity.

Development of chemo-physical processes

Project A5: Prof. Werther: Micrograding as means to increase the efficiency of soil washing

Project A8: Prof. Calmano: Wet cleaning of metal contaminated soils and characterisation of the heavy metal binding forms

Project A10: Prof. Brunner: Treatment of mixed-contaminated soil materials with carbon dioxide-water solutions and processing of the extract

Project A11: Prof. Niemeyer, Dr. Wilichowski: Post-treatment of fine-grained residuals by thermal oxidation in the steam-stripping process

Development of biological processes

Project B3: Prof. Stegmann: Treatment of contaminated soils in bioreactors

Project B4: Prof. Steinhardt, Dr. Haupt: Advanced analysis of biochemical and chemical products from petroleum degradation in soil and technical processes

Project B5: Prof. Müller: Metabolism and enzymatics of contaminant-degrading microorganisms under extreme temperature conditions

Project B6: Prof. Antranikian: Degradation of difficultly soluble contaminants by newly isolated, extremely thermophilic microorganisms

Project B7: Prof. Märkl: Use of extremely thermophilic microorganisms in soil cleanup plants

Fundamentals and evaluation criteria

Project C1: Dr. Ahlf: Ecotoxicological assessment of soil contaminations by means of biotests

Project C10: Dr. Gerth, Prof. Förstner: Future usability of arsenic and chromium contaminated soil of trickling fields

Project C12: Prof. Schneider: Prognosis and emission potential of arsenic and chromium from a trickling field under consideration of the spatial variability of the water unsaturated zone

Scientific fundamentals of process development

Project D4: Prof. Matz: Fast on-site analysis

Project D5: Prof. Francke, Prof. Voß: Synthesis of isotope labelled aromatic compounds and microanalytical examinations of contaminated soils; indirect and kontinuous dehalogenation of chlorinated pollutants

Project D6: Dr. Michaelis: Chemical interaction of petroleum contaminations and their degradation products with the humus fraction of soils

REMEDIATION OF CONTAMINATED RESIDUE FROM THE CHLOR-ALKALI INDUSTRY, WITH ELEMENTAL MERCURY, BY USING AN ELECTROLYTIC PROCESS

L. Sobral[1], J. Thöming[2]

[1] Centre for Mineral Technology - Rio de Janeiro - Brazil, Rua 4, Quadra D, Cidade Universitária, Ilha do Fundão, CEP 21941-590, Rio de Janeiro - Brazil,
[2] Technical University of Hamburg-Harburg, Dept. of Environmental Technology Eissend. Str. 40, D 21073 Hamburg, Germany e-mail: thoeming@tu-harburg.d400.de

Key words: electrolysis, extraction, heavy metals, mercury, oxidation, physico-chemical processing, waste processing

SUMMARY

Since methylmercury poisonings became apparent in Japan 40 years ago and were attributed to consumption of highly contaminated fish, a number of nations have significantly reduced reliance on mercury. We are not aware of another element whose use has been so curtailed on grounds of protection of public health and the environment.

In the United States, use of mercury has fallen 80% from a peak thirty years ago. Of remaining U.S. use, the U.S. Bureau of Mines estimated during 1993, one-third went to chlorine production; 15% to wiring and switches; 12% to measuring devices; 7% to lighting such as fluorescent bulbs; 6% to dentistry; and the remaining 27% to many other smaller uses. While all these undoubtedly confer value to society, most have mercury free alternatives, which can be marketed as environmentally kind.

During the 20th century, production of chlorine, the building block of the chemical age, became the principal use. The 381 mercury cell chlorine plants in the world are estimated to account for 40% of world mercury use .

Brazil and other countries as such, face environment contamination of soils, water streams and leaving species by mercury. For instance, the gold mining industry, that uses elemental mercury during the gold amalgamation from gravity concentrates, releases residues substantially contaminated by this element, consisting of an environment contamination source. As another concurrent to this contamination one can mention the chlor-alkali industry, that produces hydrogen, sodium hydroxide and sodium hypochlorite. In this industry elemental mercury is used as a cathode, producing, during the production process, sodium amalgam. This amalgam is further decomposed producing sodium hydroxide and regenerating elemental mercury to electrolytic cell.

During to recent approaches to different chlor-alkali facilities, in Brazil and Germany, some sources of mercury emissions to the environment were identified. Among them we can mention the soluble mercury species (Hg^{2+}), in liquid effluents, insoluble products, generated during the treatment of contaminated brines (hydroxides), as well as

residues from the electrolytic cells, graphite electrode scraps etc. However, there is a growing concern in replacing this conventional technology by using diaphragm cells, in which cation exchange membranes are used in more sophisticated reaction systems. Nevertheless, with the continuing use of the conventional process, residues and effluents are being produced and storaged. The residues exposed to climatological conditions are prone to suffer the bacteria action which come into operation releasing soluble species of mercury, providing the prompt contamination of the reception bodies.

This study aims at defining safe conditions for treating high mercury content residues (≥ 6 g kg^{-1} of residue), from the chlor-alkali industry, by an electrolytic process. This process will make use of the conventional aqueous sodium chloride electrolysis for generating oxidant species and then dissolving elemental mercury, in the bulk of the reaction system. The soluble mercury species ($HgCl_4^{2-}$) generated are simultaneously deposited at the graphite cathode surface making the decontamination feasible. This study will also comprise a thermodynamic approach of the process as a whole and, additionally, the influence of some process parameters such as sodium chloride concentration, pH and current densities.

ASSESSMENT OF PROPERTIES IMPROVEMENT OF CEMENT-BASED SOLIDIFIED DREDGED SLUDGE.

M. Boutouil, D. Levacher

Université du Havre, L.M. Groupe de Recherche en Génie Civil, Quai Frissard, B.P. 265, 76055 Le Havre, France

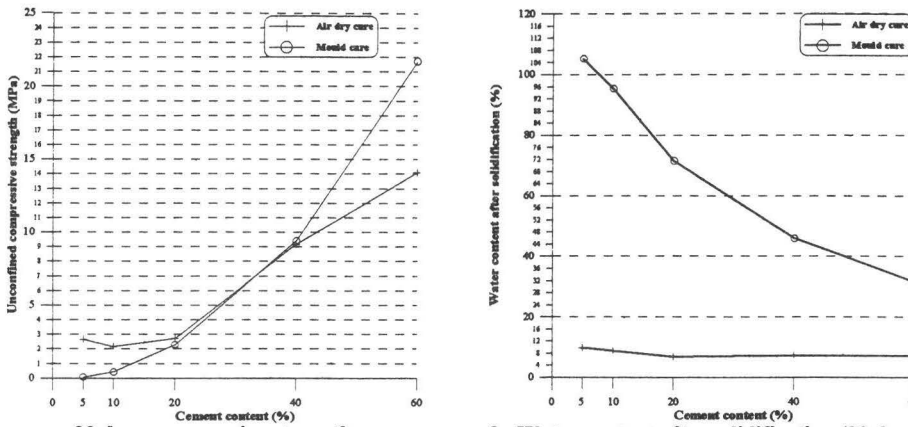
Key words : cement, compressive strength, dredged material, porosity, sludge, solidification, treatment.

SUMMARY :
In this paper the emphasis is on civil engineering parameters at prospect of assessing the possibilities of physical and mechanical improvement of dredged sediments by cement based-solidification/stabilisation. The investigations are performed to evaluate the effect of several parameters such as : nature of cement, cement content and curing conditions. It was found that the compressive strength is mainly influenced by the replacement level of cement and the curing conditions. For the specimens cured without preventing loss of water, the compressive strength has dropped notably after immersion in water. Up to 20 % of replacement cement, the important water content after solidification of mould cured specimens seems to lead to a lower compressive strength. The compressive strength was observed to be related to the ultrasonic velocity and the porosity of the solidified air cured specimens.

MATERIALS :
The previous study (Boutouil et al., 1997) has shown the effect of initial water content of the raw sludge on the compressive strength of solidified sludges. In this study only one sludge from Le Havre Harbour (France) was used. It seems to have two main characteristics. The first one is the important fine fraction (85 % of silt and 10 % of clay) and the second one is the high initial water content (152 %).
As for the cements, three cements were used : two CPA 52.5 with different C_3A and SO_3 contents, and a CPJ 32.5 which is characterised by 18 % of fly ash addition.

MAIN RESULTS :
In addition to the nature of cement, five cement contents (5, 10 , 20, 40 and 60 % by wet mass) and two curing conditions : with and without preventing loss of water, were the study parameters. The analysis of the effect of these parameters was made up to assess the key properties that supply basic informations on the matrix of the solidified sludge. The figure 1 shows the relationship between the 90 days compressive strength and the water content after solidification. The latter was calculated to draw near the amount of water in excess of complete hydration water. Broadly, the compressive strength increases with increased cement. However it can be noted that for low replacement level cement ($\leq$ 20 %), air dry cured specimens gave a better compressive strength than that of mould cured specimens. This seems to be due to the important water content after solidification of mould cured specimens (figure 1-b).
Despite a compressive strength of 2 to 15 MPa (figure 1-a), the air dry cure (with loss of water) has resulted in a specimen very sensitive to water. From table 1, it can be seen that the compressive strength is subjected to a drop up to 80 %. In the case of air dry

cure, the hydration was probably inhibited and impeded by the great loss of water. The water content after solidification were about 8 % while it has reached 100 % for the specimens solidified with 5 % of cement and cured in moulds.



a- 90 days compressive strength b- Water content after solidification (90 days)

Figure 1 : Development of 90 days compressive strength and water content after solidification against cement content

	% of cement content	UCS before immersion (MPa) 113 days	UCS after immersion (MPa) 113 days + 7 days in water
CPA Air dry cure	20	3.34	**0.69** → drop of 79.3 %
	40	6.87	**3.91** → drop of 43.1 %
	60	10.43	**3.58** → drop of 65.7 %
CPA Mould cure	20	2.14	**1.95** → drop of 8.9 %
	40	8.80	**6.87** → drop of 22 %
	60	17.23	**14.64** → drop of 15 %

Table 1 : Unconfined compressive strength before and after immersion in water.

For the specimens cured without preventing loss of water, the compressive strength was found to be related to the ultrasonic velocity and the porosity of the solidified specimens. As for the effect of the nature of cement, it was clearly perceptible beyond 40 % of replacement cement.

CONCLUSIONS :

From the results of this study, the following conclusions can be made :

- Cement content and curing conditions have a great influence on compressive strength.
- The UCS of air cured specimens was found to be very sensitive to water immersion.
- To obtain high UCS with low cement content and mould cured specimens, water content after solidification must be lowed.

The research program under study at present aims to evaluate the feasibility of immobilisation by solidification/stabilisation of contaminated sludge with cements and additives.

REFERENCES :

Boutouil M., Levacher D., Cement-based solidification of dredged material, *International Conference on Contaminated Sediments*. Rotterdam, The Netherlands. September 7-11, 1997, pp. 324-331

REMOVAL OF HEAVY METALS FROM CONTAMINATED SOILS BY COMPLEXING AGENTS

R. Kiefer, W. H. Höll

Forschungszentrum Karlsruhe, ITC-WGT, Hermann von Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany

Key words: complexing agents, decontamination, heavy metals, soil remediation

Decontamination processes for heavy metal contaminated soils so far reported in the literature have shown some considerable disadvantages. The application of strong mineral acids leads to the dissolution of carbonates or clay minerals[1]. Thus, all natural functions of the soil will be destroyed. Also the use of concentrated HCl, as a strong mineral acid, causes serious corrosion problems. Complexing agents such as EDTA[2] and NTA[3] can selectively dissolve heavy metals from soil. However, with these chemicals a secondary pollution is generated. EDTA is listed as environmentally hazardous[4], whereas NTA, although biodegradable[5], cannot be removed by normal water treatment processes[6]. These problems can be avoided by using complexing agents which are found in nature such as amino acids[7]. Corresponding to this consideration tartaric and citric acid have been applied in the investigations reported here. These chemicals are available in sufficient amounts and in various degrees of purity. Furthermore both acids and their heavy metal complexes are biodegradable[8, 9].

An on-site process has been designed in which the contaminated soil is treated with citric or tartaric acid in a first step to mobilize the heavy metals. In a second step the heavy metals / metal complexes are separated from the liquid phase by means of an ion exchange resin. The liquid phase can be recycled. The heavy metals might be removed from the regenerate of the resin by electrolysis, if the concentrations are high enough and the recovery is economic[10].

Column experiments were performed to study both the time and the volume of solution to elute the mobile fraction of heavy metals. The results indicate that the elution of heavy metals is slow. There is a rapid decrease of the heavy metal concentration within 20-50 bed volumes. However, 200-300 bed volumes of solution are necessary to elute the mobile fraction completely as shown in figure 1.

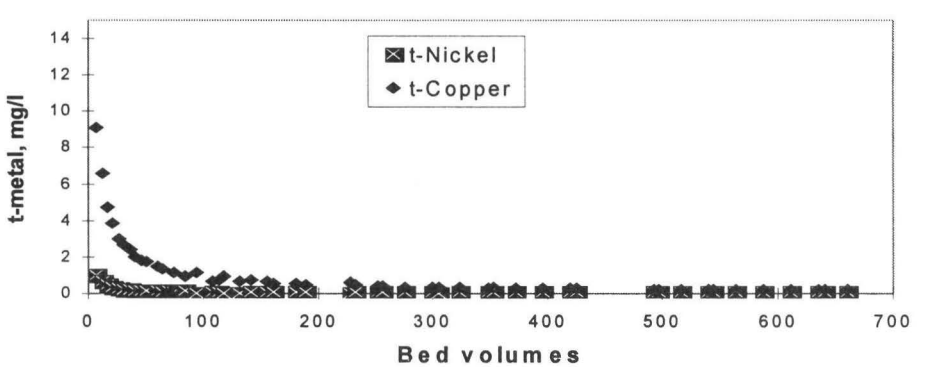


Figure 1: tCu and tNi in the effluent. Eluant: tartrate

Further column experiments were carried out to demonstrate the entire process including the elimination of heavy metals by means of a chelating cation exchanger. It was found that the separation of the heavy metal complexes by the ion exchanger (IE) resin was the rate controlling step for the process. By choosing the proper flow rate it was possible to almost completely eliminate the heavy metals. However, about 500 bed volumes of recycled solution were required to reach a steady state. The results of an experiment are shown in figure 2.

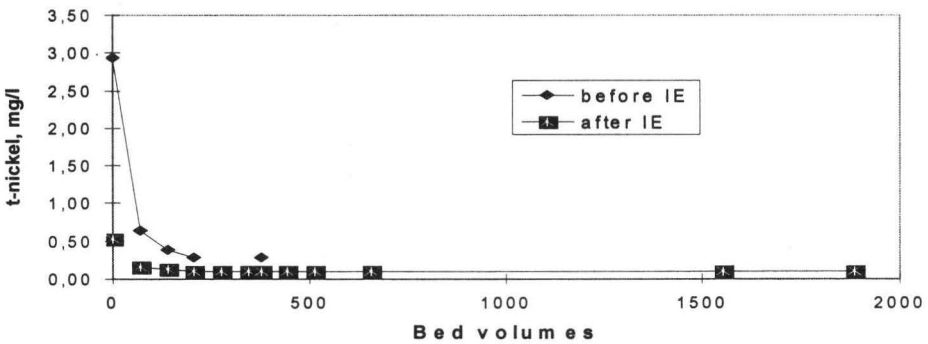


Figure 2: tNi in the effluent. Eluant: citrate

As a result the heavy metal content in soils and, therefore, their pollution is decreased considerably. The soils tested so far have been taken from a site contaminated primarily with copper and nickel. Table 1 shows the remediation efficiency related to the content of heavy metals before the soil was treated with tartaric or citric acid, respectively. The total content of copper in the soil was 570 mg/kg and that of Nickel was 105 mg/kg, determined by means of aquia regia treatment.

Table 1: Remediation efficiency. Eluant: Tartaric acid/citric acid

	Copper	**Nickel**
Final content, mg/kg	171 / 189	60 / 53
Percentage of total content	70 / 67	43 / 49

References:
1 Müller, G. and Riethmeyer, S. *Chemiker-Zeitung* 1982, 106 (7/8), 289-292.
2 Brown, G. A. and Elliott, H. A. *Water, Air and Soil Pollution* 1992, 62, 157-165.
3 Dehnad, F. *WasserAbwasser Praxis* 1993 (1), 48-50.
4 Höll, W. H. *Vom Wasser* 1995, 84, 251-261.
5 Roos, H.-J. Dissertation RWTH Aachen, 1995.
6 Brauch, H.-J. and Schullerer, S. *Vom Wasser* 1987, 69, 155-164.
7 Leidmann, P.; Fischer, K.; Bieniek, D.; Nüßlein, F. and Kettrup, A. *Chemosphere* 1994, 28 (2), 383-390.
8 Francis, A. J.; Dodge, C. J. and Gillow, J. B. *Nature* 1992, 356 (3), 140-142.
9 Francis, A. J.; Joshi-Tope, G. A. and Dodge, C. J. *Environ. Sci. Technol.* 1996, 30 (2), 562-568.
10 Langenfeld, E. *CAV* 1996, 29 (12) , 14-18.

IN SITU ATTENUATION OF HEAVY METAL MOBILITY IN CONTAMINATED SOIL BY THE USE OF PAPER MILL SLUDGE

Petruzzelli G., Barbafieri M., Bretzel F. and Pezzarossa B.

Institute of Soil Chemistry C.N.R., via Corridoni 78, 56125 Pisa (Italy)

Key words: in-situ remediation, heavy metals, mobility, adsorption, sludge

ABSTRACT

Application of paper mill sludge to soil of an old landfill, characterized by high levels of heavy metals, produced a relevant decrease (from 30% to 50%) in heavy metal mobile fractions both at laboratory and field scales. The effect was ascribable to the increase in the sorption processes of the soil matrix mixed with the sludge, describable by a Langmuir type equation.

INTRODUCTION

Soil contamination by heavy metals represents one of the main environmental risk due to the non biodegradability and persistence of these elements.

Generally the degree of contamination and clean up procedures are based on the total metal content, but mobility and bioavailability of metals must be considered when the potential of transfer through the soil profile to ground water quality and the quality food chain are concerned.

To tackle the problem of mobility of heavy metals in contaminated sites a new definition of contamination (1) based both on total and mobile species concentrations and new soft remediation procedures (2) have been developing.

Most clean up techniques for the remediation of polluted soils are very drastic and generally destroy their chemical and physical properties. A possible alternative solution is the addition of materials capable of reducing heavy metal mobility, without negatively affecting soil properties, to the contaminated soil. This procedure seems particularly suitable where large scale pollution is to be treated.

Taking into account the economic considerations a growing interest is dedicated to the possibility of the reuse of waste materials which need to be evaluated for their ability to provide a beneficial support in soil remediation

A study was undertaken to evaluate the feasibility of the application of paper mill sludge to reduce heavy metal mobility in a contaminated soil, both at laboratory and field scales.

MATERIALS AND METHODS

The sludge derived from the water treatment system of paper industry and was composed of 50% of organic matter (extremely fine fibres and waste debris from the wood preparation stages), talc, $CaCO_3$ and clay from the paper production units. Heavy metals are present only at negligible level. The soil derived from an old landfill was characterized by high levels of heavy metals (Table 1) and pH 7.1.

At field scale paper mill sludge was mixed with soil at a rate of 30% and a depth of 1.5 m, according to the Italian legislation. Before treatment and six month after sludge application to soil heavy metal mobile fractions were determined by a sequential extraction procedure (H_2O, KNO_3, EDTA) previously devised for the characterisation of contaminated sites

(Petruzzelli et al., 1993). This procedure allows the evaluation of water soluble, exchangeable and adsorbed or complexed metals in soil.
Adsorption experiments on soil, where Zn and Cd were used as heavy metal models, were carried out before and after treatment according to a procedure previously reported into details (Petruzzelli et al., 1994).

RESULTS AND DISCUSSION

Six months after the treatment the sequential extraction procedure carried out on soil samples collected in the field showed a relevant decrease (from 30% to 50%) in heavy metal mobile fractions. Some results are reported in Table 1.

TABLE 1 - EDTA extractability of heavy metals in original soil (os) and after addition of paper mill sludge (pms). Data are expressed as mg kg^{-1}.

METAL	TOTAL CONTENT	EDTA os	EDTA pms
Cu	975	195	126
Zn	2500	400	232
Ni	110	3.52	2.46
Pb	1150	94.6	46.3
Cd	23.6	15.6	9.65

At laboratory scale adsorption experiment showed that for both metals isohterms can be classified as "L type" and were describable by a Langmuir type equation.

TABLE 2 - Sorption maxima (qm) of Langmuir equation in original (os) and treated soil (pms).

METAL	qm (μg/g)
Zn os	26.1
Zn pms	38.4
Cd os	18.4
Cd pms	23.9

The results indicated that after the addition of paper mill sludge to soil the solid phase showed a greater affinity for both metals (Table 2).
A possible explanation for these findings is that new sorbing sites become available on the solid phase of soil following the paper mill sludge addition. This sludgeitself has relevant sorptive properties being a significant source of organic matter on which heavy metals are able to strongly sorb.
Therefore, the reduction of heavy metal mobility in the field can be also ascribed to the increase in the sorption ability of the soil matrix mixed with the paper mill sludge.
Although the experiments do not represent long term field trials, they show the potential for use paper mill sludge in reducing heavy metals mobility. The material would be promising for 'in-situ' immobilisation of heavy metals in contaminated soils. Further investigations are needed to test the long term resistance of paper mill sludge to chemical weathering, microbial degradation or lowering of pH.

AKNOWLEDGMENTS

Authors thank L. Lubrano for his excellent technical assistance.

REFERENCES

1) Barbafieri M., Lubrano L. and Petruzzelli G. (1996). Ann Chim. 86, 585.
2) Gupta S.K., Vollmer M.K., Krebs R. (1996). Sci Tot. Environ. 178, 11.
3) Petruzzelli G., Lubrano L., Giovannini G., Lucchesi S., Cervelli S. (1993). In: F. Arendt et al. (eds) *Contaminated Soil*, 545.
4) Petruzzelli G., Lubrano L., Petronio B.M., Gennaro M.C., Vanni A., Liberatori A. (1994) J. Environ. Sci. Health, 29, 31.

LIFE PROJECT 96ENV/DK/16, "CLEAN UP OF POLLUTED SOIL - ENVIRONMENTAL/ECONOMIC EVALUATION AND OPTIMISING OF IN-SITU TECHNIQUES "

Lars Deigaard, Soeren Toft Nielsen

Scanrail Consult, Pilestraede 58, 1112 Copenhagen K, Denmark.

Key words: chlorinated hydrocarbons, cost-benefit analysis, environmental impact, guidelines, hydrocarbons, in-situ remediation, models.

INTRODUCTION

The Danish National Railway Agency has initiated a development project centred on environmental/economic evaluation and optimising of in-situ techniques. The project describes the total environmental costs and benefits from remediation actions. It is part of the Danish National Railway Agency's general environmental action plan.

The project is supported by the LIFE-program from the European Economic Community. The purpose of the LIFE-program is to contribute to the development and implementation of the European Economic Community politic for environmental issues. The program is administrated by the LIFE committee at the European Commission DGXI.

The project is financed by the LIFE committee (50%), the Danish National Railway Agency (45%) and the Environmental Protection Agency of Denmark (5%). The budget amount to approx. 1.4 mill GBP.

Scanrail Consult is responsible for the project management, and the project is run in co-operation with the consulting engineers HOH Water and Environment Ltd., Nellemann, Nielsen & Rauschenberger Ltd., and the auditor Panell Kerr Forster.

The project was started on March 1st, 1997 and the final results are expected by March, 2000. The results will be presented in a report and at a seminar in Copenhagen.

GENERAL DESCRIPTION OF THE PROJECT

The aim of this project is to achieve effective and environmentally optimal remediation of soil and ground water at sites contaminated with oil and organic solvents.

A decision-making model for use in choosing the best method of remediation for a given situation will be developed and verified. Furthermore, the clean-up methods applied will be optimised. The model will be developed based on the in-situ remedial measures at five different sites. The sites are polluted with oil or chlorinated hydrocarbons.

The project is expected to produce the following results:

- development of a decision-making model for optimal restoration of soil and ground water
- preparation of guidelines for an all-inclusive environmental accounting, which can also be applied to a variety of other clean-up projects.
- optimisation of in-situ remedial methods
- remediation of five contaminated sites in Denmark

The decision-making model will make it possible to base clean-up decisions on all relevant aspects. The project adds a new dimension to traditional cost-benefit analyses, in so far as it also takes into account the environmental cost of the various clean-up methods.

The total environmental benefit and impact of selected clean-up methods will also be described. The environmental benefits will be calculated in accordance with the established practice for risk analysis. The environmental impacts will be made in accordance with the principles for life-cycle assessments.

The decision-making model will provide a useful tool for any public or private organisation faced with the problem of cleaning up a site contaminated by oil or chlorinated hydrocarbons.

The project employs a comparative analysis in which various remedial methods will be tested, optimised and subjected to cost-benefit evaluations. A full account of the environmental impact of each clean-up method will be included in each analysis, and the remedial method chosen will be optimised in each case.

HYDROCARBONS CONTAMINATED SOIL REMEDIATION USING SOIL VENTING. APPLICATION OF SIMULATION MODELS

Alberto Bonilla, Pedro Cuesta, Roberto Zubiaga, Beatriz Hierro

CITMA (LABEIN Technological Research Centre)
Cuesta de Olabeaga, 16, 48013 BILBAO-SPAIN

Key Words: Clean-up technologies, decontamination, remediation, soil vapor extraction (SVE), vacuum extraction, petrol hydrocarbons, Volatile Organic Compounds. VOCs, computer simulations, simulation model

Spills from underground storage tanks are one of the most common sources of soil contamination by hydrocarbons. Chemical implied in hydrocarbon spills combine its toxicity with the high risk due to its volatile nature (acummulation, explotion, hazards, etc.) and with its high mobility (the compunds are very volatile, BTEX are partially soluble in water,...). These aspects are specially important, from the point of view of risk, when the polluting source is placed inside or near of an urban area.

One useful technology to remediate this soils is the technology known as soil venting or soil vapor extraction (SVE). This involves an air extraction from the unsaturated zone on which volatiles compounds are distributed among the liquid phases (aqueous and non-aqueous liquid phases) and the soil gas phase. The soil gas extraction will reduce the volatile compound concentration in gaseous phase displacing the equilibrium to the evaporation of volatile compounds. Circulation of clean air will increase these process.

Soil present two zones clearly distinguised: the saturated zones (below the water table) and the unsaturated zone (over the water table). Materials present at the unsaturated zone can be found in three phases: solid phase (basically soil particulate), liquid phase (non aqueous phase liquid and aqueous phase) and gaseous phase (air and volatile compounds). Interchange phenomena (disolution, evaporation, adsorption, ...) would be produced among these phases.

The parameters for the liabitity and efficiency of venting process are numerous. These parameters are relationed with physical-chemical properties of contaminants (vapor pressure, solubility, Henry law, ...), with the soil characteristics (air flow permeability, porosity, residual suturation, organic matter content, ...) and with the specific features of contaminated site (distribution of contaminants, water table location, ...). This evidences the complexity to define matematically the soil contamination behavior, complexity that get worse when we take in consideration a non-equilibrium state as existing when a venting process take place.

There are several simulation models (of different complexity) which allows to explain the existing soil situation and the way to incide the process in order to make it more effective. concentrations, kinetics, etc.)

Contaminated Soil '98, Thomas Telford, London, 1998, 1143–1144

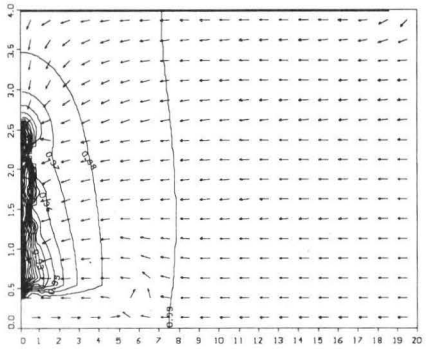


Figure 1. Air Flow

In this framework. in order to optimize the system design and the venting process two models have been applied to a specific hydrocarbons contaminated soil. The studied site was formed by an old petrol station (in operation when the study was carried out) located near the centre of an urban area. Excavations carried out in the sorroundings made to suspect about hydrocarbons spills. In order to confirm this possibility and to define the real situation and risk present a characterization an risk assessment study was carried out.

This article gathers up the results and conclusions obtained after the application to this site of two venting process simulation models: Hyperventilate model and Airflow-SVE.

Hyperventilate model confirms the feasibility of SVE technique for site remediation. For a remediation time of 1 year, the acceptable removal rate has been estimated in 27,4 Kg/day. The achieved removal rate has been estimated in 67 Kg/day. The model proposes a number of 10 extractions wells, that means an influence radius of 5-6 meters.

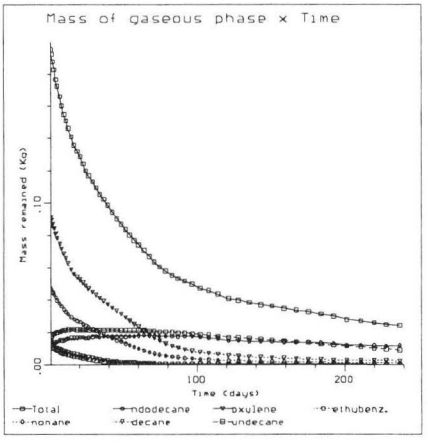


Figure 2
Remanent mass in gas phase

Airflow-SVE model estimates a radius of influence of 6-7 meters (see fig. 1). This radius implies a number of 8 extraction wells. The model estimates a high and fast removal of volatile compounds (BTEX). Aproximately 120 days before the start of process these compunds will be totally removed (see fig. 2). These data aim to the use of a carbon filter during the first process steps and a compost filter after that. The model estimates the practically total removal time in 240 days. Remanent contaminants will be the less volatile contaminants. Removal of this will be enhanced by biodegradataion process enhanced by the soil air flow. This aspect is not contemplated by the model. Remanent contamination is mainly placed on the water table fluctuation zone (see fig. 3).

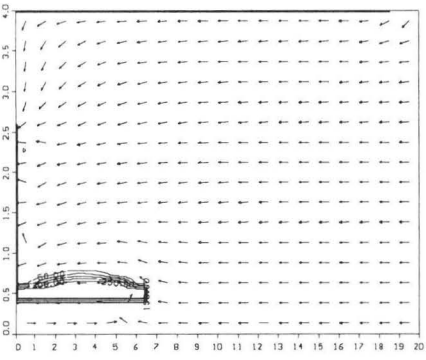


Figure 3.
Distribution of the remanent contaminants

WILLOW CLONES FOR SHORT ROTATION COPPICE ON HEAVY METAL CONTAMINATED LAND

I.D.Pulford[1] and D. Riddell-Black[2]

[1] Environmental Chemistry, University of Glasgow, Glasgow G12 8QQ
[2] WRc plc, Medmenham, Marlow, Buckinghamshire SL7 2HD

Key words: in-situ bioremediation, heavy metals, contaminated soil, clean-up technologies.

SUMMARY

Twenty clones of willow (*Salix* spp) were grown on soil highly contaminated with heavy metals as a result of sewage sludge disposal over a period of more than 50 years. Using wood and bark concentrations of metal, the clones could be split broadly into two groups: those which took up relative high amounts of Ni and Cu, and those which took up relatively high amounts of Zn and Cd. The high Ni/Cu uptakers had very poor survival rates and produced little biomass, whereas the other group showed high survival and biomass production rates. This differential response to heavy metals may allow selection or breeding programmes to provide the basis for management options for coppice systems based on particular metal contamination problems.

INTRODUCTION

Short rotation willow coppicing of heavy metal contaminated land has a number of attractions as a management option: 1) it can produce an economic return on the land; 2) it can screen the land and prevent access; 3) it can reduce losses by wind-blow and leaching. In addition, it will contribute to the production of renewable energy for which targets of about 15% per annum are now set. There is concern that insufficient agricultural land of good quality will be available for this use, and so derelict and contaminated land becomes an attractive alternative. The large number of willow clones already available, and being added to by breeding programmes in the UK and Sweden, provide a wide range of options for reclamation.

MATERIALS AND METHODS

A randomised block design experiment with three replicates was established in 1995 on soil which had elevated levels of heavy metals due to prolonged sewage sludge disposal (typical values were 30 mg Cd /kg; 1500 mg Cr /kg; 800 mg Cu/kg; 500 mg Ni/kg; 700 mg Pb/kg; 2000 mg Zn/kg). Metal concentrations in wood and bark tissue were measured. A visual assessment of biomass productivity was made using a scale of 1 (little or no growth) to 5 (good, even growth to 1.5 - 2 m).

RESULTS AND DISCUSSION

Table 1: *Visual assessment and heavy metal content of bark (based on low< 400 mg Zn /kg>high: low< 20 mg Cd, Cu or Ni / kg>high) of 1 year old willow (Salix spp).*

Willow name	Visual assessment	Zn	Cd	Cu	Ni
S. viminalis Lysta 699	1.7	low	low	high	high
S. triandra x viminalis Q83	2.3	low	low	high	high
S. viminalis Jor	1.7	low	low	high	high
S. burjatica Germany	5.0	high	high	high	low
S. aurita x cinerea x viminalis Rosewarne White	5.0	low	high	low	low
S. viminalis Orm	3.0	low	low	high	high
S. caprea x viminalis Coles	4.0	low	low	high	high
S. viminalis Tora	1.3	low	low	high	high
S. viminalis Jorunn	3.7	low	low	high	high
S. spaethii	4.7	low	low	low	low
S. aquatica Gigantea	1.7	low	low	high	high
S.candida	4.3	low	high	low	low
S. caprea x viminalis x cinerea Calodendron	4.7	high	high	low	low
S. viminalis Ulv	2.0	low	low	high	high
S. cinerea x viminalis x cinerea Othery Moor	4.7	low	high	low	low
S. aurita x cinerea x viminalis Delamare	4.7	low	high	low	low
S. viminalis Bjorn	2.3	low	high	low	low
S. triandra Black Maul	1.0	high	high	high	high
S. dasyclados	5.0	high	high	low	low
S. eriocephala Mawdesley	2.0	low	low	high	high

The pattern of heavy metal uptake in the different clones shows the basis for possible management options when selecting willow for short rotation coppice of contaminated land. Considering only those clones with an assessment of 4.0 or better, *Salix spaethii* took up low amounts of all four metals and so would be suitable for screening and stabilising a site with little uptake of metal. *S. aurita x cinerea x viminalis* (Rosewarne White), *S.candida*, *S. cinerea x viminalis x cinerea* (Othery Moor) and *S. aurita x cinerea x viminalis* (Delamare) took up low amounts of all metals except cadmium. Only *S. burjatica* (Germany) gave good biomass yield coupled with high metal uptake, except for Ni. Nickel seemed to be the most phytotoxic of the metals, although *S. caprea x viminalis* (Coles) did combine high Ni (and Cu) uptake with good yield. *S. viminalis* (Jorunn) also had high Ni and Cu but its yield assessment of 3.7 was just below the cut-off value.

Based on a small number of clones and only four metals, there does seem to be sufficient variability within *Salix* clones to allow selection for specific types of remediation. Further work is needed to breed new clones combining metal uptake with good yield. Information on the response to other important heavy metals is required.

Title: INDEX FOR BENEFICIAL USE ON SOILS (IBUS)

Randall E. James, Ph.D.

Ohio State University Extension, P.O. Box 387, Burton, Ohio 44021, USA

Key words: limiting values and standard values, mixed wastes, prevention, quality standards, ranking system, risk mangement, soil protection, target values

Most people working in the waste management arena think about particular products or waste streams. Each product is viewed, discussed, evaluated and often regulated as a uniquely different material unrelated to other waste products. However, in today's world, waste products are routinely comingled and it is becoming increasingly difficult to evaluate each possible combination independently. There is a real need for a standard rating system to produce comparisons between the wide variety of waste products and possible combinations.

The Index for Beneficial Use on Soils (IBUS) system is a one page check list that is designed as a rough screening tool. It helps determine whether or not a particular waste product should be considered for land application without substantial monitoring and/or regulations. The system also provides a useful educational tool for students, regulators, and waste managers. In addition, it helps farmers and the general public understand the various risks, benefits, and management requirements for any material that is proposed for beneficial use on soils.

The system is partially based on the United States, Environmental Protection Agency Part 503 rule which describes the term exceptional quality (EQ) biosolids. According to the rule, EQ biosolids should be considered acceptable for land application with little or no additional regulation. Due to the extensive risk assessment research that went into the development of the Part 503 rule, it is reasonable to use the standards set for EQ biosolids in creating a general standard for comparison with any waste product.

The IBUS system does not address application rate, which should be determined on the appropriate agronomic or horticultural uses of the material. The system also does not address questions surrounding the volumes of material coming from a single generator. Even the most benign material can cause environmental problems in a particular area, if huge volumes are generated. It does however, provide a simple framework for decision makers to begin to sort out the potential beneficial use of the confusing array of individual and comingled products being generated today. It also brings to the forefront issues that should be resolved before a product is applied to the soil.

BIOLOGICAL REMOVAL OF WOOD PRESERVATIVE (PCP) WASTES IN SOIL. AUTOCHTHONOUS MICROFLORA AND EFFECT OF COMPOST ADDITION

Gorostiza, I.; Susaeta, I.; Bilbao, V.; Díaz, A.I.; San Vicente, A.I.; and Salas, O.

CITMA (GAIKER), Parque Tecnológico. Edf. 202. 48170 Zamudio, SPAIN

Keywords: biodegradation, chlorinated hydrocarbons, microbial activities, compost.

Pentachlorophenol (PCP) has been widely used in many industrial applications as antiseptic, herbicide, pesticide, and wood preservative. Its dispersion into the environment, specially soil and water, represents a risk not only for the human health but also for the ecosystems. PCP is highly toxic and in fact is included by the USEPA in the "priority pollutants" list (Keith and Teillard, 1979). This chlorinated compound is described as rather recalcitrant, only being biodegraded by a limited number of microbial groups. Among them strains of *Arthrobacter, Rhodococcus chlorophenolicus, Streptomyces rochei, Pseudomonas* y *Flavobacterium* have been described (Resnick & Chapman, 1994).

The aim of this work is to assess the potential of the autochthonous microflora of a non contaminated soil for the biodegradation of PCP. Besides, the effect of the addition of a supplement carrying degrading microorganisms (compost) on the biodegradation rate was studied.

Soil preparation

A non contaminated sandy loam soil was selected and characterized. The results of the more relevant parameters of this soil are presented in Table 1. A sufficient amount of soil was artificially contaminated with an industrial waste (sawdust from an anti-blue-stain bath in a sawmill) containing PCP (1.8 %). The amount of waste to be added to the soil was determined through a couple of tests indicating toxicity to the soil microflora. Microtox™ assays and respiratory activity tests (biometer flasks) were carried out on different waste:soil mixtures. The maximum tolerable concentration determined by these tests (data not shown) was waste:soil 0.3 % (fw/fw), which represents 55 ppm of PCP in soil.

Parameter	Result
pH	7,73
WHC (%)	30,3
CEC (mEq/100g)	18,8
Clay (%)	13,3
Silt (%)	13,8
Sand (%)	71,9
Classification (ISSS)	Sandy loam
Total aerobes (cfu/g)	$2{,}0 \cdot 10^7$

Table 1. Soil characterization results

Biodegradation assay

Soil microcosms tests were carried out in aerated columns (Figure 1) filled with a waste:soil mixture at the maximum tolerable PCP

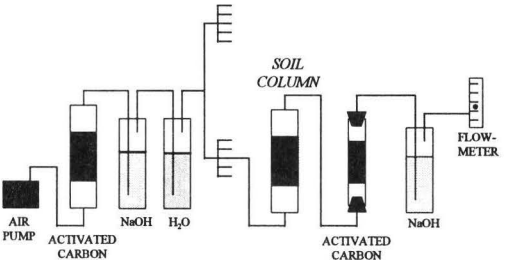


Figure 1. Aerated column system flux diagram.

concentration (55 ppm). Control columns filled with clean soil were also run. At time intervals, soil samples were taken from columns and PCP concentration were analyzed. Besides, this system allows us to quantify PCP disappearance due to volatilization, monitor biological activity (respiration), and follow microbial populations.

The results of the biodegradation tests are shown in Figure 2 as mean of two replicate columns. No PCP was detected in the activated carbon traps at the air exhausts, so no correction for volatilization was necessary. The kinetic parameters (first order) for PCP biodegradation are $K = 0.109\ day^{-1}$ and $t_{1/2} = 6$ days (calculated between experimental days 28 and 56).

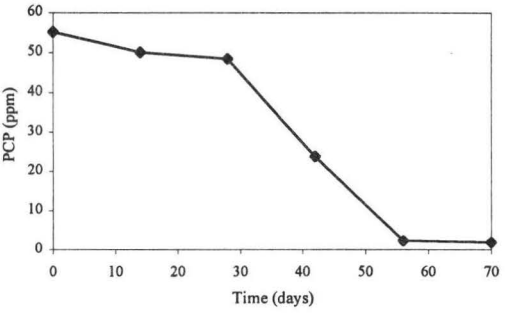


Figure 2. PCP biodegradation curve.

Effect of compost addition

Respiratory activity tests were carried out to estimate the influence of compost addition on the PCP biodegradation rate. Soil was amended with compost at a 1:1 ratio. Figure 3 shows the cumulative CO_2 released in each case. Controls without waste were run in every case. As can be seen, the respiration rate of compost is much higher than that of the soil. Amended soil (1:1) shows an intermediate activity. In all cases the presence of the waste (0.3 %) enhances the respiration rate. Considering the increase in respiration due to the presence of PCP in each condition (supposed to be related to PCP biodegradation) it can be observed that PCP degrading potential of compost is considerably greater than that of soil alone. Nevertheless, the addition of compost was noteworthy (1:1), so it would be necessary to evaluate the cost derived from this practice.

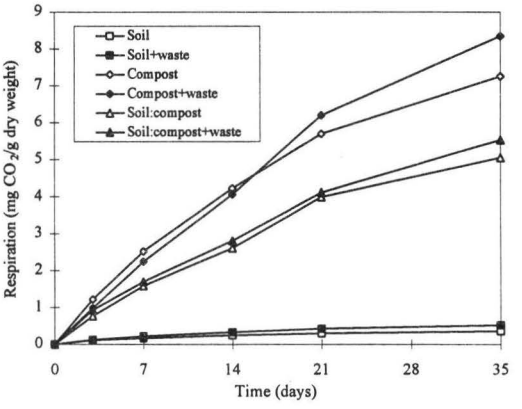


Figure 3. Effect of compost addition. Cummulative CO_2 curves.

Acknowledgements

This work is a part of a project financed by IHOBE, S. A.

References

Dasappa, S. M. & Loehr, R. C. (1991). *Wat. Res.* **25**: 1121-1130.
Keith, L. H. & Telliard, W. A. (1979). *Environ. Sci. Technol.* **13**: 416-423.
Resnick, S. M. & Chapman, P. J. (1994). *Biodegradation* **5**: 47-54.

RECOVERY OF HCH (HEXACHLOROYCLOHEXANE) CONTAMINATED SOILS USING SOLVENT EXTRACTION TECHNOLOGIES

Salas, O; Sagarduy, M.; San Vicente, A.I.; Díaz, A.I.; de la Quintana, E. and Susaeta , I.

CITMA (GAIKER), Parque Tecnológico. Edf. 202. 48170 Zamudio, SPAIN

Keywords: HCH, solvents, extraction.

Due to former industrial activities many sites of the province of Biscay are contaminated with high quantities of HCH wastes. Treatability studies have been carried out in order to enable us a better founded decision for the implementation of solvent extraction technology and the conditions under which it should be applied. Many factors can affect the success of the selected technology in a soil recovery action, so it is important to develop lab scale treatability studies in order to reduce the risk of a direct implementation of the technology withouth previous studies.

Selected soils

Two soils were selected and characterised. Soil N and Soil SG particle size distribution and HCH content are presented in Table 1.

Soil	% Clay	% Silt	% Fine sand	%Coarse Sand	Organic Matter (%)	HCH (ppm)
N	19.3	25.3	50.1	4.8	7.67	2,464
SG	9.15	17.4	55.1	18.3	0.91	134,769

Table 1. Selected soils particle size distribution and total HCH content,

Soils were excavated ,transported and properly stored at 4 °C until used for the experiments.

Experimental set-up.

Soil were homogenised in a blender and afterwards they were air dried. Particles above 5mm were discharged and the rest of the soil was grinded.

10 grams of the grinded soil were used and 30 grams of solvents were added to each extraction vessel. After 5 minutes of gentle shaking, (in a previous step the minimum required contact time was studied, data not shown, and no differences in HCH removal were found between 5, 15, and 30 minutes) samples of the supernatant were withdrawn for HCH analysis.

In Table 2 results shows some of the different experiments that were carried out.

SOIL	WATER CONTENT	METHANOL	PROPANOL	ACETONE	MEK
N	0 %	96 ± 0.04	96 ± 0.05	93 ± 0.04	84 ± 0.04
	20%	94 ± 0.05	89 ± 0.08	102 ± 0.02	81 ± 0.05
	40 %	42 ± 0.06	66 ± 0.02	74 ± 0.07	ND
SG	0%	73 ± 0.02	95 ± 0.07	98 ± 0.07	95 ± 0.15
	20%	24 ± 0.02	106 ± 0.07	67 ± 0.02	100± 0.07
	40 %	13 ± 0.02	77 ± 0.04	22 ± 0.05	ND

Table 2. Recovery of HCH in % of the initial amount and different water contents of the soils.

A conclusion that can be withdrawn from the results presented in Table 2 is that the water content highly affects the yield of the HCH extraction. Water could avoid contact between solvent and HCH. Acetone, MEK, Methanol and Propanol have achieved their suitability for the removal of HCH in the selected soils.
Treatability studies have to be considered a key factor in the choose of solvents and conditions for the application of the proposed technology.

Residual Concentration mg/kg $_{dry}$ Sum of Isomers				
Solvent	**Methanol**	**Propanol**	**Acetone**	**MEK**
Step 1	157.02	183.95	140.44	144.32
Step 2	7.77	11.06	5.62	5.80
Step 3	0.31	0.71	0.28	0.37

Table 3. presents the residual HCH after three extraction steps in soil N.

As can be concluded for the results of Table 3 the residual concentration of HCH are very low and fulfil the legal requirements for disposal of the clean soil

Experiments in a semi-batch reactor
Fig 1. represents a semi batch reactor. The reactor was filled with 1 kg of air dried SG soil and 2 kg of acetone. In Fig 2 the extraction profile of HCH for SG soil is represented.

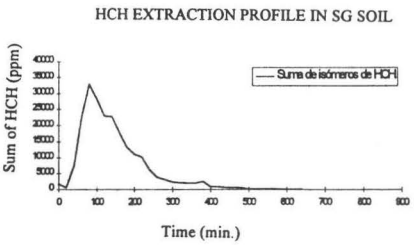


Fig.2

EXTRACTION SYSTEM

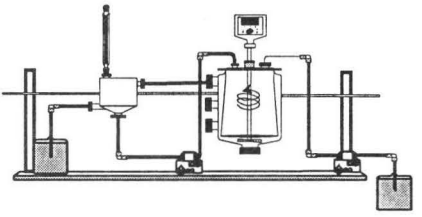


Fig 1.

Acknowledgements
This work is part of a research project financed by the PGTI program of the Basque Government.

References
Meckes, M.C. et al. (1992). *J. Air Waste Manage. Assoc.* 42: 1118-1121.
Hall, D.W. and Sandrin, J.A. (1990). *Environmental Progress* 9: 98-105.
Rawe, J. (1992). *EPA/540/R-92/016b.*

THE USE OF COST BENEFIT ANALYSIS IN SELECTING REMEDIAL OPTIONS FOR CONTAMINATED LAND

I. Martin[1], M. Lowe[2] and S. Herbert[3]

[1] Environment Agency, National Groundwater and Contaminated Land Centre, Olton Court, 10 Warwick Road, Olton, Solihull B92 7HX, UK
[2] Department of Environment, Transport, and Regions (DETR), Ashdown House, 123 Victoria Street, London SW1E 6DE, UK
[3] Environment Agency, Land Quality, Third Floor, Steel House, 11 Tothill Street, London, SW1H 9NF, UK

Key words: cost-benefit analysis, environmental management, remediation, sustainability

UK policy and legislation on contaminated land requires remedial action to be carried out where there are unacceptable risks to health or the environment, assessed in relation to the current or immediately intended use of the land and its wider environmental setting, and where there are appropriate and cost-effective methods available. Selecting an appropriate remedial strategy for a specific contaminated site is a process which involves the balancing of technical, social, economic, and other policy issues.

The focus in preparing guidance in the UK to date has been on providing a formal, transparent structure for appraising different remedial methods and has assisted in making a defensible and appropriate choice. This work has clearly outlined the decision-making procedure for setting remedial goals; and for selecting remedial strategies using technical, managerial, and cost-benefit criteria. Supporting technical documentation is being developed to assist stakeholders in the process of setting remedial objectives and in considering the technical dimensions of remedial option appraisal. However, there is also a need for guidance on the assessment of costs and benefits of different approaches. This is a key issue for those funding remediation as part of the commercial redevelopment of sites; it will also, in modified form, be a requirement for regulators imposing remediation requirements under the proposed statutory regime in Part IIA of the Environment Protection Act.

Formalised approaches of cost benefit analysis (CBA) have been used in the UK largely for the appraisal of major infrastructure projects such as London's third airport and bridges over the rivers Tay and Severn [1]. The key difficulty in applying such a quantitative approach to assessing remedial options is in assigning a monetary value to either environmental impacts or benefits, particularly when comparing approaches, for example biodegradation versus on-site containment of contamination, or their off-site disposal. There are a number of economic modelling tools, such as contingent valuation, hedonic pricing, and the use of production functions, but there is little or no experience in their application to the issues relevant to land remediation [2,3].

In response to this the Department of the Environment, Transport and Regions (DETR) and the Environment Agency commissioned a scoping study in order to identify research

groups and programmes active in environmental cost and benefit assessment with potential relevance to contaminated land remediation; and to identify practical experiences of assessing costs and benefits in land remediation projects in the UK [4].

The study concluded that many practitioners in land remediation do not fully understand the basis for considering costs and benefits in relation to the remediation of land contamination. Where cost and benefit assessments were used, the methods were informal, subjective and often not transparent. The work also suggested that the formalised CBA approach to assessing remedial options is unlikely to be practical under the conditions of the current remediation market for several reasons including:

- The complexity and resource requirements (both time and money) to carry out a formalised CBA study.
- Some environmental benefits or impacts will not be readily quantifiable in monetary terms because of their highly personal and subjective nature.
- Conversion of some impacts / benefits to a monetary value would require assumptions to made which cannot be substantiated by current scientific understanding (for example, the future toxicity of residual contamination).
- There is a danger that by valuing the environmental costs and benefits of a remedial scheme in only monetary terms, the valuation decided upon by the decision-maker on a site-specific basis, may differ substantially from the view which would be taken by a larger section of society.
- Many valuation techniques for CBA require some degree of standardisation in parameters (for example life cycle analysis). Perhaps, fundamentally, the site specific nature of land contamination prevents such methods being widely used.

Despite these difficulties, the market is innately dynamic and has previously demonstrated an ability to react positively to the introduction of other environmental management methodologies. This may enable realistic "market" valuations to emerge in an iterative manner from attempts to employ CBA methods in practice. However, this is likely to happen only over a long timescale.

Following on from this initial study the Environment Agency has commissioned further research to develop a practical methodology and to provide advice to decision-makers on the assessment of costs and benefits for remedial option selection. The work will also evaluate alternative systems to CBA including those based on multi-criteria analysis.

[1] Hanley, N. and Spash, C. (1994) Cost Benefit Analysis and the Environment. Published by Edward Elgar Publishing Ltd, Aldershot, Hampshire.

[2] Department of the Environment (1991) Policy Appraisal and the Environment: A Guide for Government Departments.

[3] Department of the Environment (1994) Environmental Appraisal in Government Departments.

[4] DETR (in preparation) The Use of Cost Benefit Analysis in Selecting Remedial Options for Contaminated Land: A Scoping Study.

APPLICATION OF THE BIOFERTILIZER MADE OF THE PRODUCTS OF AEROBIC TREATMENT OF THE WASTE WATERS FROM THE PIG-FARMS IN THE MONITORING SYSTEM OF ANTHROPOGENIC SOILS OF NORTHERN CZECHIA

I.I.Barbolina[1], I.A.Arkhipchenko[1], J.Vana[2]

[1] Research Institute of Agricultural Microbiology, Podbelsky Shossee 3, St.Petersburg-Pushkin 8, 189620, Russia
[2] Research Institute of Crop Prodaction, Drnovska 507, 16106 Praha 6-Ruzyne, Czech Republic

Key words: bioremediation, urban areas, sludge, microbial activities, phytotoxicity, crops

SUMMARY
The possibility for application of the fertilizer Bamil produced from the products of an aerobic treatment of the pig-farm waste waters for a biological recultivation of anthropogenically disturbed soils of Nothern Czechia was studied. The agrochemical microbiological and biochemical peculiarities of this fertilizer were shown. Application of Bamil activized the microbiological processes in the soil ensuring a 3-8 fold increase in the microorganism biomass, a decreased the phytotoxicity of the substrates and increased ryegrass yield on recultivated plots in 5-7 fold.

The industrial regions of North-West Czechia are the most anthropogenically contaminated areas in the middle Europe due to an intensive brown coal mining yielding an increased content of ash (20-40%), sulphur and a number of other harmful substances. In low regions where the coal minings takes place the soil is disturbed by a surface excavation and its burning at thermal power stations. The excavation from the earth cuts after the upper layer of fertile soil is taken away leaves heavy clay with 80-90% of clay content. These materials are characterized by low water-physical properties and low content of nutrient elements. Due to burning of low quality coal a great amount of ash is formed which covers and accumulates on the area of 2000 hectares. The ash is characterized by good water-physical properties although a low content of nutrient elements, phytotoxicity and by an almost absolute biological sterility. Such substrates are one of the most difficult objects for recultivation since they contain compounds toxic for plants, microorganisms, remain barren for a long time and are the sources of erosion and environment pollution. Owing to modern monitoring system these lands can be partially reclaimed and used for agriculture. For the soil reclamation of special importance is their biological recultivation directly at the sites of coal mining and burning. The decisive factor of the biological recultivation is an intensive application of the organic fertilizers . Such measures should envisage the control over the chemical, biological and sanitary-hygienic state of the soil in the recultivation process. The applied fertilizers must meet the standards on the content of especially dangerous elements, heavy metals and pathogenic microorganisms.

For such purposes the liquid manure and sewerage effluents which do not meet the requirements are usually used. For the first time the possibility of applying the biofertilizer Bamil was studied for recultivation of the soils on ecologically polluted areas. The process

of producing Bamil from the products of aerobic treatment of waste waters from the pig-farms has been developed at Research Institute of Agricultural Microbiology StPetersburg, Russia (1). The fertilizer meets the sanitary-hygienic requirements, is characterized by low content or absence of heavy metals and harmful elements, it contains a large amount of required nutrient compounds and microelements.

Our research showed that application of the biofertilizer has considerably activized the microbiological processes in the soil which is very important for restoring the microbocenoses, acceleration of the soil formation and enhancing the fertility of the reclaimed soils. Application of Bamil caused a 10-100 fold increase in the number of various groups of bacteria and fungi in the recultivated substrates. The biomass of microorganisms in the fertilized variant was 3-8 times higher that in the substrates without the fertilizers. The maximal increase in the carbon of the microbial biomass was observed after application of Bamil in the ash variants. Addition of Bamil to the ash and to the mixture of the cut out ground ensured a 7,5-fold increase in the microbial biomass, the variant of the degraded soil-ash mixture after application of the fertilizer yielded a 5,1-fold increase.

Application of the biofertilizer Bamil ensured introduction of a great amount of basic nutrient elements for the plants and microorganisms into the antropogenic soils. This revived the bacteriological activity of the soils and caused an intensive growth of the plants which leave a large number of the root leftovers. All this leads to an enhanced soil fertility and considerable acceleration of biological recultivation of the anthropogenic soils. Apart from that, the biofertilizer Bamil contains viable microorganisms represented basically by the bacteria of genus Bacillus which at the first stages of recultivation take an active part in the microbiological processes in the antropogenic soils.

An increase in the biomass and in the amount of soil microorganisms correlated with an enhanced yield of ryegrass in the Bamil variants. Application of the fertilizer ensured a 5-7 fold increase of the yield as compared with similar variant where no fertilizer was used. The maximum yield was observed when Bamil was applied together with ash. The effectivity of Bamil was showed also in its aftoeffect after 1 year.

1. Arkhipchenko I.A., Miller V.V. (1992) Method of manufacture of biologically active sludge. Patent No. 1757209 A, Russia

This work was financed by the Ministry of Science and Technology of Russia within the frames of the international project «Microbial communities»

DECREASE IN THE SOIL POLLUTION IN ANIMAL BREEDING INDUSTRIAL AREAS USING THE METHODS OF MICROBIAL ECOTECHNOLOGY.

I.A.Arkhipchenko[1], M.A.Alekseyev[2]

[1] All-Russia Research Institute for Agricutural Microbiology,
189620, St.Petersburg-Pushkin, Podbelskogo str. 3, RUSSIA
[2] State Architectural-Civil Engineering University, 198005,
2-nd Krasnoarmeyskayay str. 4, St.Petersburg, RUSSIA

Key words: agriculture, fertilizer; microorganisms, microbial activities, organic matter, oil products.

SUMMARY
A process for production of microbial fertilizers from the animal breeding and poultry wastes has been developed. The prospects for application of these fertilizers for enhancing the soil biological activity, increasing the yield and quality of plants and decreasing the oil bearing pollutions in the soils are shown.

During the recent years in the region of the Baltic Sea an industrial animal and poultry breeding has been developed. At present 16 poultry plants are located around St.Petersburg. There are 12 mln hens and 3 pig-farms (each of them comprising from 24 to 35 thousand). The total volume of the poultry dung is 10 mln/year and the pig manure - 1.3 mln t/year. The content of the organic pollutants is within 20 - 40 g/l. This seriously endangers the environement especially the soil, water and ground basins. The organic wastes entering the soil disturb the biological balance of the system inhibiting the microflora and the plant growth, they also cause an autrtofixation of the basins.

An ecotechnology for processing the animal breeding wastes has been developed with the use of microorganisms for producing effective pelleted biofertilizers and purified wate water suitable for dumping. The technology is based on the use of active microorganism strains capable to oxidize the organic wastes under aerobic conditions.

A wide scale practical application of this technology will make it possible not only to remediate the soil but to obtain up to 40 thousand of fertilizers from the poultry dung and 15 thousand of biofertilizers from the animal farm wastes.

Thus, not only the ecological problems will be soloved but principally novel types of fertilizers will be obtained. They combine positive qualities of the minerals (absence

of weed seeds, known chemical composition, low application dose) and organics (2-3 year action , making the soil healthier and enhancement of its biological activity).

The mineral fertilizers are characterized by a high content of nitrogen (3.5 - 5%) and phosphorus (2 - 3%), they also conntain a considerably high amount of physiologically active compounds which are stimulants for the plant growth, are capable of making a healthier soil and inhibit the microflora: fusariosis vectors, potato scab, clubroot of crucifers. All this not only encreases the product quality but its yield (by 70-80%). It has been observed that these fertilizers effectively ensure degradation caused by the oil pollution, a 5-6 fold increase in the biological activity of the soils under recultivation. The ecologically clean products have a considerable yield increase (from 60 to 120%).

At the same time the biological activity of the soil cenosis has a 1.5-2 fold increase and the microbila biomass a 2-3 fold.

The microbial association of the biofertilizers is rather diverse, in its basis there are microorganisms of genus Bacillus, Nocardia- and corryneiform bacteria. It is very effective for
degrading the oil bearing pollutions of the soil. It is known that with an oil pollution a sharp change in the carbon to nitrogen ratio in the direction of an abrupt increase in the carbon occurs. Due to the fact that the microbial fertilizers are characterized by a high content of nitrogen and high bilogical activity the process of the oil pollution destruction in our experiments proceeds at a high rate and is within 53 - 66% depending on the applied dose of the fertilizers. As we established, the titer of the microorganisms oil-destructors is $2x10^4$ CFU/g of biofertilizers. The oil oxidizing microflora comprises the cultures of microorganisms capable of utilizing, as a sole source of carbon and energy, various fractions of oil and its derivatives right down to the heaviest one - the fuel oil.

The feasibility calculations for a large-scale production of biofertilizers (10 thousand tons/year) are presented. It has been determined that at a sales price 400 $ per ton the net profit of the enterprise will amount to 1.2 mln $ per year which corresponds to the production profitability 65.6%.

In 1994 the present development was accorded the status of the Foundation "Eureka" (Brussels).

The present work is financed by the Ministry of Science and Technology of Russia within the frames of the project "Bioconversion of Wastes"

DEFINING THE RADIUS OF INFLUENCE IN A BIOSPARGING PILOT TEST

Maurizio Buzzelli and Marco Gavinelli

Ambiente S.p.A., via R. Fabiani 3, 20097 S.Donato Milanese (MI) - Italy

Key words: field test, geoelectrics, petrol hydrocarbons, vadose zone monitoring

In order to remediate an aquifer located in an agricoltural area, polluted by petroleum hydrocarbons, a Biosparging pilot test has been carried out.
Short term pilot tests have been used to obtain specific information on the behaviour of injection wells under a given set of geologic and engineering conditions.
The radius of influence has been defined using a low flow rate (110÷120 l/min at a pressure of 0,5 bar) to add oxygen into the groundwater with a biosparging injection well. The goal was to biodegrade dissolved and adsorbed hydrocarbons in the phreatic aquifer avoiding the stripping of the low boiling compounds. The test has been carried out following two different approaches: continuous and pulsed mode.
Four monitoring systems led to a good estimation of the radius of influence:

a) Geophysical monitoring of the radius zone using Electrical Resistance Tomography
b) In situ Dissolved Oxygen
c) Measurement of the concentration of O_2, CO_2 and He (used as tracer).
d) Water table mounding

a) ERT Test

A cross-borehole electrical resistance tomography has been used to depict the principal regions of air flow in the saturated zone surrounding air sparging wells.
An automated data acquisition system measured the resistivity of the subsurface soil through the installation of piezometers constructed with copper ERT electrodes placed in the wells AS1 (14 electrodes), MW1A, MW2A, MW3A (16 electrodes respectively) as shown in figure 1 and 2.
Planes AS1-MW1, AS1-MW2, AS1-MW3 and the three-dimensional block AS1-MW1-MW2 have been considered for the tomographic reconstruction.

b) Dissolved Oxygen Distribution

Dissolved oxygen concentration has been measured every 2 hours in four piezometers (MW1A, MW2A, MW3A, MW4A). This survey helped to define the radius of influence and showed the presence of residual air saturation.

c) O_2, CO_2 and He Measurements.

Air with 1 percent helium was injected for 20 hours. Soil gas samples were collected over time (at 2 hours interval) from probes installed in the vadose zone. The extend of air diffusion in the vadose zone has been defined as 9.4 m from the injection point.

d) Water Table Mounding

The water table is displaced when air is injected into the satured zone. The movement of this displaced water can lead to a rise in the water table. Such an action can be used as an indicator of the radius of influence of the sparge well.
Combining the results obtained monitoring all of the above mentioned parameters it has been possible to define the exact extension of the Radius of influence in the vadose and satured zone.
In the surveyed site the elevated permeability of the soil gave insignificant results about mounding monitoring.

Contaminated Soil '98, Thomas Telford, London, 1998, 1159–1160

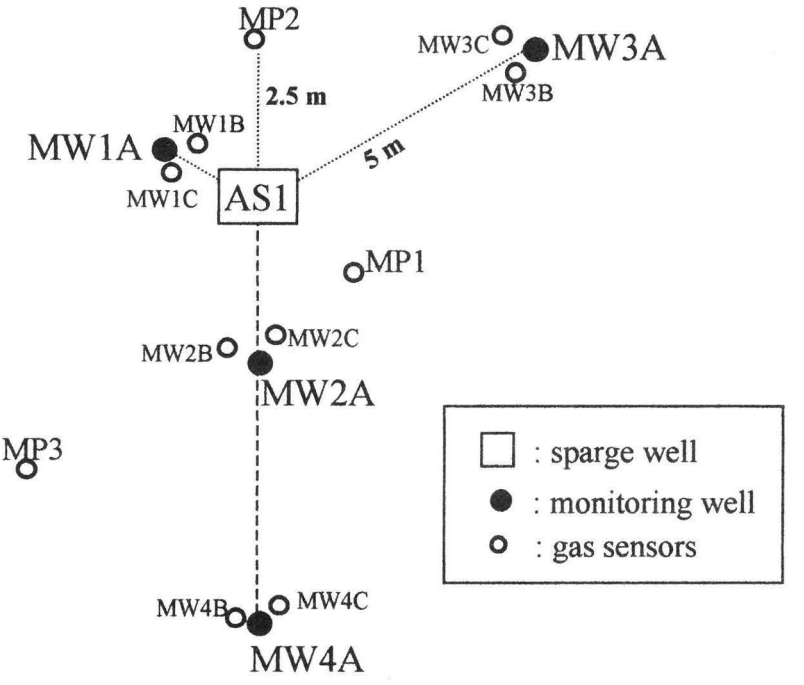
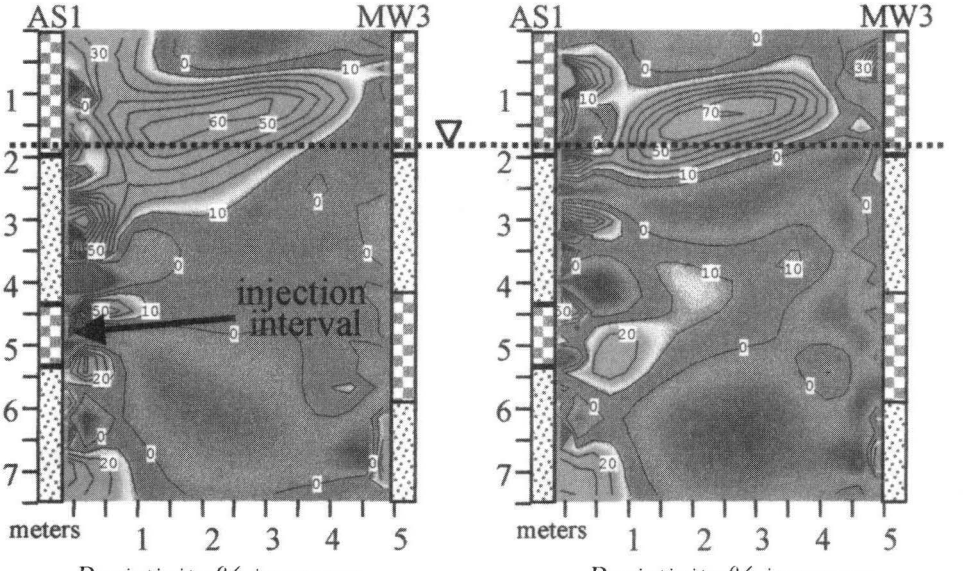


Figure 1 : Well locations at the site



Resistivity % increase after 3 hours of sparging

Resistivity % increase after 6 hours of sparging

Figure 2 : ERT Cross Sections

ELECTROEXTRACTION OF HEAVY METALS BY ELECTROMEMBRANE PROCESS

D. Hassen-Khodja, F. Persin, J. Sandeaux, R. Sandeaux and C. Gavach

Laboratoire des Matériaux et Procédés Membranaires, UMR 5635, CNRS, 1919 route de Mende, F-34293 Montpellier Cedex 5, France

Key words : Electrodecontamination, electroextraction, contaminated soil, ion-exchange resin, ion-exchange membrane, copper ion.

Summary

Soil contamination by the industrial activities represents in all countries a serious threat to the environment. For soils polluted with heavy metals, many studies have shown that the electrokinetic techniques are promising cleaning methods. The aim of this work is to develop a decontamination process using regenerating cations which migrate under an electrical field through ion-exchange membranes. The present study consists of two parts. Electroextraction of cations was carried out, on the one hand from a soil model constituting of a cation-exchange resin in Cu^{2+} form and on the other hand, from a soil sample taken of an area contaminated by chemicals (Cu, Cr, As) from the wood impregnation industry.

Experiments were performed with a laboratory cell composed of five compartments separated by ion-exchange membranes, as schematically represented in Figure1.

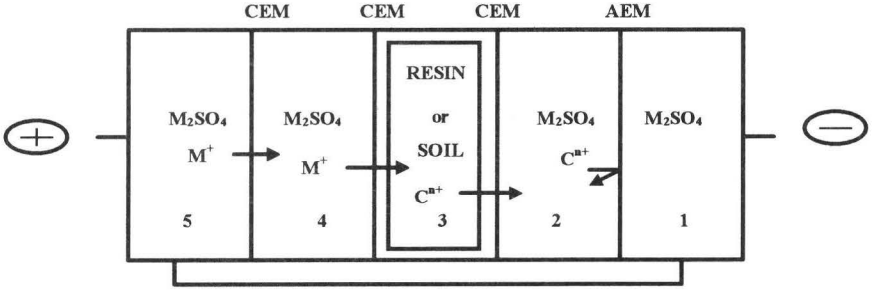


Figure 1. Schematic representation of the laboratory cell.

The resin or soil was introduced into the central compartment (3) in which it was sandwiched between two cation-exchange membranes. Under an applied electric current the regenerating cations (M^+) migrate toward the cathode through the cation-exchange membrane from the feed compartment (4) to the resin or soil where they are exchanged with the contaminant cations (C^{n+}). These latter cations which can also cross a cation-exchange membrane, are concentrated in the receiver compartment (2) since they don't cross the anion-exchange membrane separating the (2) and (1) compartments. The (1) and (5) compartments are electrode compartments, they are connected to avoid the pH variations due to the electrode reactions.

The experiments using a fine-grained sulfonic resin (C265 H, Rohm & Haas) were performed by using the following regenerating cations : Na^+, K^+, NH_4^+, H^+, which migrate through cation-exchange membranes under various current densities (1, 5, 10 $mA.cm^{-2}$). The Cu^{2+} extraction ratios were higher with the Na^+ and K^+ regenerating cations (70-80%).

The soil studied is sandy, basic (1). It contains a significant amount of organic matters and inorganic cations as Na^+, K^+, Ca^{2+} cations which enter in competition with the electrotransport of contaminant cations (Cu 2.3g.Kg^{-1}, Cr 1.7 g.Kg^{-1}, As 1 g.Kg^{-1}). The NH_4^+ ion, sligtly acid, was used as regenerating cation. The current density was 0.36 $mA.cm^{-2}$. The extraction ratio of Na, K, Ca, Cu obtained from 0.7 Kg of soil treated during 3800 hours were about 4-10 % for the first experiment. A second experiment was performed under similar experimental conditions, except the pH in the receiver compartment which was maintained at a higher value between 8-9. In Figure 2, the amount of extracted copper, expressed in mg, was plotted versus time for the two experiments. It can be seen that a basic pH in the receiver compartment increases significantly the copper extraction. That can be due to a complex formation between copper and ammonium, $Cu(NH_3)_n^{2+}$ [2].

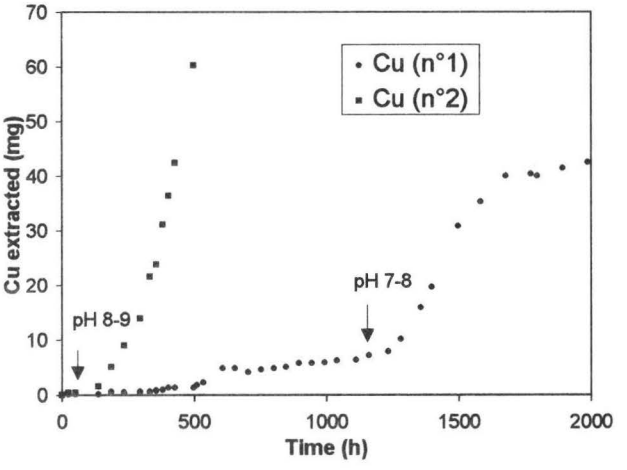


Figure2. Variation with time of Cu extracted amount (mg) in the receiver compartment for the experiments n°1 and n°2.

Electro-osmose was observed from the the (3) to (2) compartment in the experiments performed using resin, and from the the (4) to (3) compartment in the experiments performed using soil.

REFERENCES

[1] Persin F., Toularastel T., Sandeaux J., Sandeaux R., Gavach C, Etude préalable à la décontamination d'un sol pollué par un produit de traitement du bois (Cu, Cr, As), III International Conference on the Biogeochemistry of Trace Elements, Paris, Mai 1995.

[2] Kratgen J., Atlas of metal ligand equilibria in aqueous solution, Ed. Ellis Korwood limited, 1978.

Support of the Efficient Handling of Contaminated Sites by the AlfaWeb Information System

Werner Geiger, Matthias Reißfelder and Rainer Weidemann
Forschungszentrum Karlsruhe, Institut für Angewandte Informatik
Postfach 3640, D-76021 Karlsruhe, Germany

Keywords : contaminated sites, knowledge transfer, databases, software tool, regulations, public

Introduction

For an efficient handling of contaminated sites, the respective technical information has to be made available to the persons in charge at their working place. In this contribution, the WWW-based technical information system on contaminated sites, AlfaWeb, is described. In the AlfaWeb information system, a large number of technical reports and databases of the State Institute for Environmental Protection Baden-Württemberg for the handling of contaminated sites are contained. This information as well as appropriate search facilities are offered by Internet, Intranet and CD-ROM.

Technical Information on Contaminated Sites Contained in AlfaWeb

The AlfaWeb project is aimed at developing a technical information system for the handling of contaminated sites and making available this information and the respective search facilities via Internet, Intranet and CD-ROM (Geiger et al., 1997). The development is performed within the framework of the GLOBUS project on behalf of and in cooperation with the Ministry for the Environment and Transport and the State Institute for Environmental Protection of Baden-Württemberg.

The system contains all currently relevant manuals and technical reports published by the State Institute for Environmental Protection for the handling of contaminated sites. It comprises the guidelines and manuals for the recording, assessment and remediation of contaminated sites, e.g. a guideline for the investigation of the groundwater. Furthermore, it contains actual reports on partial aspects of the handling of contaminated sites, e.g. a report on microbiological methods for the remediation of contaminated sites. These reports comprise a total of more than 8000 printed pages with about 2000 figures.

Furthermore, the RefAS and the BOBAN databases have been integrated into the system. RefAS is a database with references to already performed remediations of contaminated sites. BOBAN contains data on stationary and mobile soil treatment plants. In addition, the system contains further information, such as regulations and laws which are of relevance for the handling of contaminated sites.

The above reports and databases are converted into a net of HTML pages and GIF files by means of conversion programs. For access to the information in the HTML and GIF files, an access system with various access paths and search facilities has been developed:

- With an "access via reports" the user can access information according to the hierarchical structure of the reports.

Contaminated Soil '98, Thomas Telford, London, 1998, 1163–1164

- With an "access via fields of work" technical information spread in various reports and databases can be accessed systematically according to the various fields of work during handling of contaminated sites.
- A keyword search offers access to the reports via a list of keywords on contaminated sites. In order to enable this kind of search, keywords have been added to all reports and parts of reports.
- In the full text search, one or several arbitrary search terms can be entered by the user. This search is performed directly in the report texts.
- In the reports, hyperlinks are provided for cross references among the reports. These cross references offer rapid access to technical background information.

Supply of Information to Different User Groups

A central objective of system development was to make available both the information and access system directly at the working place of the potential user groups. The various user groups, however, have different possibilities to access computers and computer networks. To solve this problem, the information and search facilities are offered via both the Internet and the administration Intranet of the state of Baden-Württemberg and via CD-ROM:

- Via the Internet, technical information on contaminated sites is offered to engineering offices, persons working in other technical fields and the interested public with access to this computer network. The system is made available to these user groups on the publicly accessible WWW server of the Ministry for the Environment and Transport of Baden-Württemberg (http://www.UIS-extern.um.bwl.de/).
- Via the administration Intranet of the state of Baden-Württemberg, the authorities with access to this network have access to its technical information without being exposed to the data protection risks that are usually associated with an Internet connection. The system is made available in the administration Intranet on an internal server of the State Institute for Environmental Protection.
- Via the CD-ROM, the engineering offices, authorities and other interested parties not yet connected to the Internet/Intranet are provided with the technical information. This version of AlfaWeb may also be applied by frequent users of the system to avoid the often unacceptable response time in the Internet. The CD-ROM version offers PDF files of the reports in addition to the HTML and GIF files such that the reports can be printed out completely or partially by the user himself.

In the first six months of 1997, more than 200 000 accesses were made to the files of the Internet installation. This demonstrates that there is a considerable need of technical information on contaminated sites and that this need can be satisfied and dissemination of this technical information can be improved by the use of modern information and communication technologies.

References

Geiger, W., Reißfelder, M. and Weidemann, R. (1997) Distribution of expert information on contaminated soil via Internet, Intranet, CD-ROM and print media, in K. Alef et al. (eds.) Eco-Informa '97, Eco-Informa Press, Bayreuth, pp. 72-77.

INVESTIGATION AND REMEDIATION OF A SOLVENT SPILL ON THE CHALK OUTCROP OF SOUTHERN ENGLAND

K. Blackmore[1], Dr L. Clark[1] and P. Sims[2]

[1] WRc plc, Henley Road, Medmenham, Marlow, Buckinghamshire, SL7 2HD, UK;
[2] ERM Ltd, Eaton House, Wallbrook Court, North Hinksey, Oxford, OX2 0QS, UK (formerly WRc).

Key words: Groundwater remediation; organic contamination; soil vapour extraction; purification of exhaust air.

Summary

Following the implementation of a new stock control system at a chemical factory, located on the Chalk outcrop of Southern England, leakage of solvent from an underground storage tank was suspected. The leak was traced to a pipe flange (during testing of the tanks), the volume of solvent lost was unknown but was estimated to have occurred over a 3 year period. In 1994, WRc were asked to investigate the site and a phased approach was adopted, consisting of a soil gas survey followed by intrusive drilling. A total of 37 soil gas probes were installed in the vicinity of the known leak and an area of possible solvent contamination was identified. Subsequent shell and auger drilling demonstrated that contamination of the Chalk was concentrated in a relatively small area of the site.

While groundwater contamination has occurred, the bulk of the solvent contamination lies within the top 15 metres of the aquifer, in the unsaturated zone; the 'putty' like nature of the Chalk below the site has limited solvent migration.

A total of 24 groundwater sampling points located around the site have been used to demonstrate that groundwater contamination from solvent is localised, and restricted to a small area of aquifer around the original contamination source.

A programme of pump and treat was initiated in July 1995 and has operated since then, providing both hydraulic control (so preventing off-site migration of contaminated groundwater) and a mechanism for removing solvent-contaminated groundwater. Treatment of the abstracted groundwater with activated carbon proved necessary until May 1996, after which time levels of solvent were sufficiently low that further treatment became unnecessary. Significant improvements in groundwater quality have been observed during the remediation programme.

To address the unsaturated zone contamination, a vacuum extraction system was designed. Seven purpose designed boreholes were installed for vapour extraction with a further eight boreholes installed for hot air injection. A catalytic oxidation system was installed to treat the vacuum extraction off-gas prior to its release to the atmosphere.

The first full scale vacuum extraction plant was commissioned in November 1995 and successfully removed over 13 000 kg of solvent, before it was replaced with an upgraded system in October 1996. Trials undertaken during the first phase demonstrated that the Chalk did not possess uniform permeability and that increased mass removal rates could be achieved under higher vacuum conditions. The design of the upgraded system therefore allowed for increased vacuums to be selectively applied. The current system has removed over 100 000 kg of solvent.

The upgraded system also allowed the re-use of the hot, treated air exiting the catalyst by re-injecting it into the ground. A trial of hot air injection ran from June to August 1996, with permanent hot air injection started in December 1996. While the practice has resulted in an increase in ground temperature, and abstracted air temperatures, no enhancement in the solvent removal rate has yet been observed.

All of the remediation plant and pipework has been installed so as to facilitate future redevelopment of the site.

In summary:

- a programme of groundwater abstraction is successfully providing hydraulic control, preventing off-site migration of contaminated groundwater, as well as providing an effective mechanism for removing contaminated groundwater and;
- the vacuum extraction system is successfully reducing the mass of residual solvent remaining in the unsaturated zone.

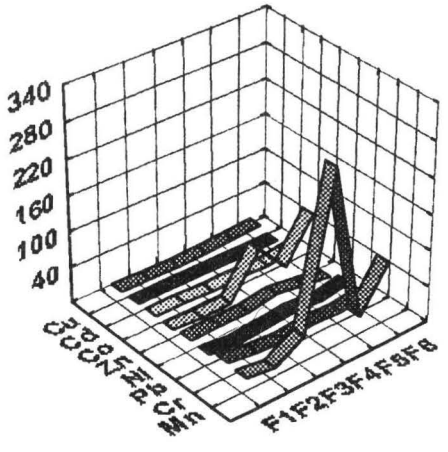
THE SEQUENTIAL EXTRACTION OF METAL FORMS IN THE SOIL OF THE BESKID ZYWIECKI IN POLAND

Nowak Barbara, Siobowicz Grażyna, Łukasik Krystyna *, Sołtysiak Grażyna*

Silesian University of Medicine, Department of Toxicology, 41-200 Sosnowiec, Jagiellońska 4, Poland
***Institute for Ecology of Industrial Areas40-833 Katowice, Kossutha 6,Poland**

The major focus of this investigation was determine chemical forms in soil for different places in Beskid Zywiecki (Poland). Sequential extraction enables the determination of the fraction of individual form of element in the soil (exchangeable F1, carbonate F2, Mn-oxides F3, Mn-Feoxides F4, organic F5, residual F6). Soils located at Beskid Zywiecki (CIECINA, CISIEC, ZABNICA) sampled during 1991/1992 were examined. One sites were localised in „clean" region (ZABNICA) and the remainder near a roadway and railway station . CIECINA and CISIEC are a small mountain village in Beskid Zywiecki in the southern Poland (non-industrial region). The local emission source is the roadway where average traffic intensity is about 164 cars per 60 minutes. One way ANOVA analyses were performed to investigate the influence of sample location (roads, railway, „clean"). We obtained differ essentially for Pb (0.0083) and Cu ($p = 0.0019$). Tessier [1] fractions of particular metals in soil for three locations are shown below Fig.1-3.

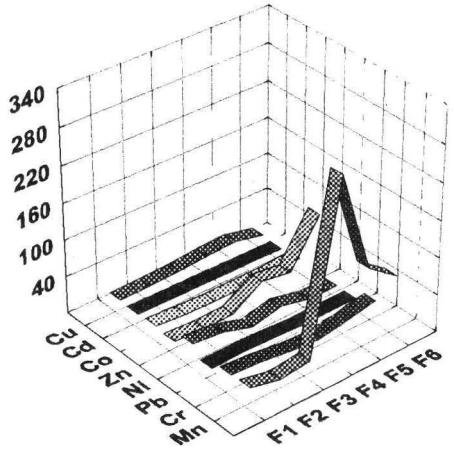
Fig.1.Sequential extraction in Soil in Beskid Zywiecki (CIECINA_WAY)
[micro g/g]



F1 exchangeable, F2 carbonate, F3 Mn-oxides
F4 Mn-Feoxides, F5 organic, F6 residual

Fig.2.Sequential extraction in soil in Beskid Zywiecki -Cisiec3

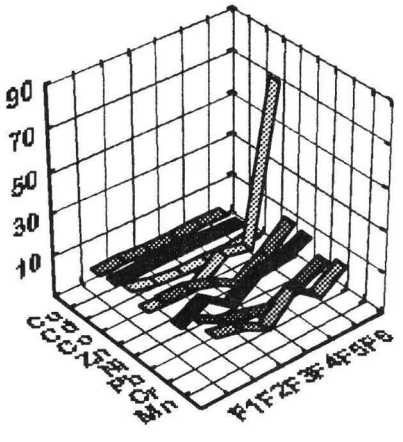
[micro g/g]



F1 exchangeable, F2 carbonate, F3 Mn-oxides
F4 Mn-Feb oxides, F5 organic, F6 residual

Fig.3. Sequential extraction in soil in Beskid Zywiecki-Zabnica.

[micro g/g]



REFERENCES

1 Tessier A., (1984), Trace metals in oxic lake sediments possible adsorption onto iron oxyhydroxides, *Geochem. Cosmochim. Acta, 49*, 183-194 .

KEYWORDS: chemical forms in soil, One way ANOVA analyses

ASSISTERIX - a TNO Software Product for Soil Protection at Industrial Sites

Dik de Weger, M.Sc.
TNO-MEP, Dept. of Industrial Safety, P.O. Box 342, 7300 AH APELDOORN
(Netherlands)
Tel +31 55 549 3812, Fax + 31 55 549 3390, E-mail d.deweger@mep.tno.nl

Keywords: pollution prevention, soil protection, risk assessment, decision support system, industrial sites.

Introduction

In the posters presented around the Dutch "Directive for Soil Protection of Industrial Sites", the Decision Support System for Soil Protection Strategy of Industrial Sites (acronym: BBB) has already been introduced. The system is a risk based instrument, facilitating the process of selecting the optimal soil protection strategy in which private companies and the competent authorities are commonly involved.

In order to enhance the use of the Decision Support System, a computerised version has been developed under the name ASSISTERIX. This acronym stands for Assessment of Industrial Site Terrestrial Risks, and is a precise explanation of the main features of the system:

- a decision support aid (ASSist);
- meant for Industrial Sites;
- assessing TErrestrial RIsX.

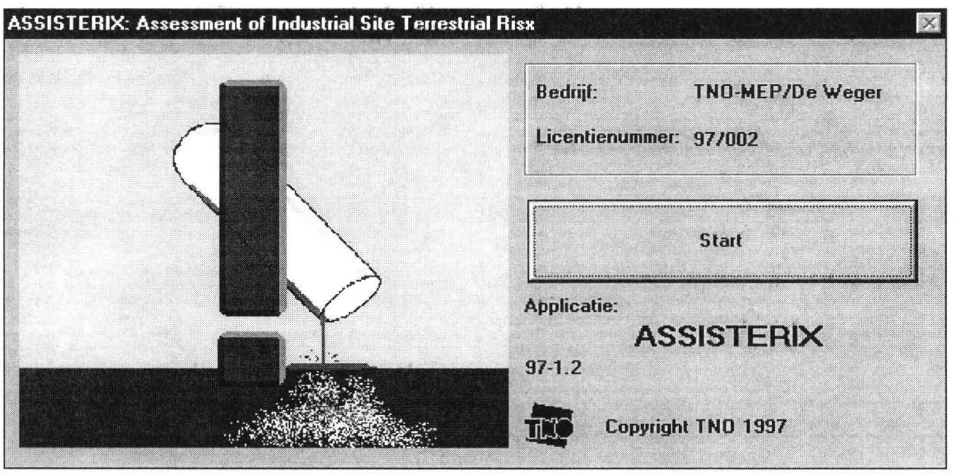


Figure. *Introduction screen of the TNO software package ASSISTERIX*

The software package

ASSISTERIX is a user friendly computer tool, running under Windows 3.x or Windows 95, which simplifies the decision support methodology in an intelligent way. Apart from providing a tool for filing soil risk data of specific companies and/or individual facilities, the system contains a database with the parameters needed for the risk calculations. However, the key feature of ASSISTERIX is the support the system provides when establishing the soil risk score for a specific industrial facility, taking into account soil protection measures (implemented and/or planned ones).

When using ASSISTERIX, one is led through the programme so as to avoid choices that are not supported by the Decision Support System (Dutch Guidelines). At each stage of application of the Decision Support methodology, only those options (precautionary measures) are shown that are relevant in that specific situation. The calculations that are necessary to determine the pollution size score are carried out by the system based on substance or location properties in the database. To this end, the programme includes a substance database containing all the parameters necessary to carry out the calculations;

The system has been equipped with several useful functions. For example, the industry's identified activities or sub-activities may be marked with a company-specific code and description; this is to facilitate recognition of the (sub)activities when using the programme or the software output. The company's administrative data (name, address, etc.) can be entered and stored in the system. Furthermore, a reporting facility is included into the programme which allows for printing overviews of the risk scores and categories of the individual installations and the company as a whole. And finally, the programme has been provided with an extensive help-function.

During the introduction of the Dutch Directive for Soil Protection Strategy, ASSISTERIX was adopted as the tool supporting the implementation of the Guidelines. ASSISTERIX is to be used by the local and regional authorities responsible for delivery of permits, and by problems owners such as controllers of landfills, polluted sites etc. (including industries and authorities).

In the Netherlands, several industrial sectors have already started the development of a branche-specific version of the Decision Support System. In the meantime, these specific checklists have been incorporated into ASSISTERIX, resulting in ASSISTERIX-PLUS. The wording used in ASSISTERIX-PLUS has been adapted to the terminology for the specific installations and facilities used in these branches. ASSISTERIX-PLUS includes checklists for the following sectors:

- metal and welding industry;
- dairy industry;
- textile and tapestry production;
- graphical industry;
- chemical industry.

DECISION SUPPORT SYSTEM FOR SOIL PROTECTION OF INDUSTRIAL SITES

Dik de Weger, M.Sc.,
TNO-MEP, Dept. of Industrial Safety, P.O. Box 342, 7300 AH APELDOORN
(Netherlands)
Tel +31 55 549 3812, Fax + 31 55 549 3390, E-mail d.deweger@mep.tno.nl

Keywords: prevention, soil protection, risk assessment, ranking system, industrial sites.

Background

The recently issued Dutch "Directive for Soil Protection of Industrial Sites" marks the growing interest for soil protection in the soil conservation policy of the Netherlands. As a part of this Directive, the Decision Support System for Soil Protection Strategy of Industrial Sites (acronym: BBB) has been developed. The BBB is a risk based instrument, facilitating the selection of the optimal soil protection strategy, a process in which private companies and the competent authorities both find themselves involved. The BBB can be applied for a complete plant or factory but also for individual facilities.

The BBB consists of a decision scheme which guides the user through the subsequent steps needed to establish the required level of precautionary measures and provisions (scheme below). A categorised methodology is offered, allowing for a quick soil risk estimate using a minimum of input data. The required input data are standardized and can be simply read from tables with relevant data that are included in the BBB. The model does not require complicated calculations.

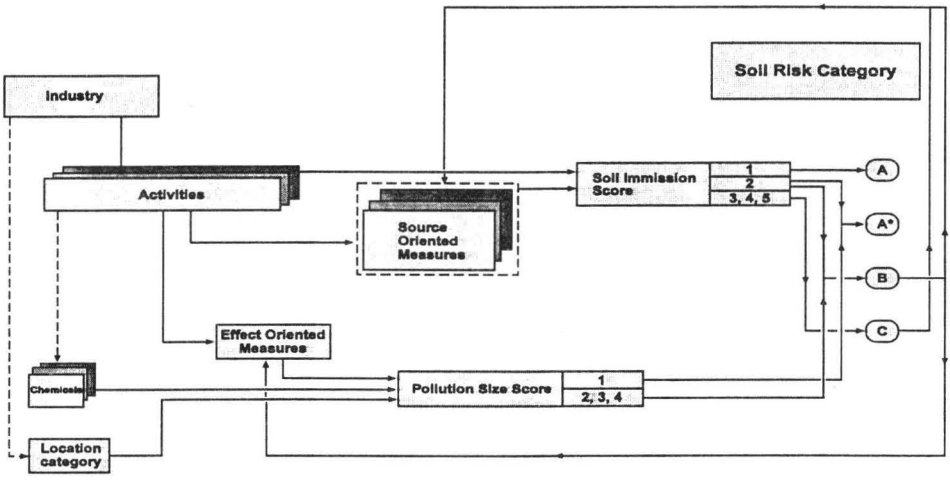


Figure. Scheme, representing the Decision Support System for Soil Protection Strategy of Industrial Sites (acronym: BBB).

Soil Immission Score

Before actually determining the Soil Immission Score, the plant is subdivided into logical units. Practical experience has shown that the various types of activities in an industrial plant form a practical lead. In the BBB, the following activities are distinguished:

- storage of bulk liquids;
- handling and internal transport of bulk liquids;
- storage and handling of bulk cargo (solids) and packaged goods;
- process installations;
- other (sewer systems, workshops, emergency collection tanks, waste water treatment facilities).

Soil Immission Scores have been established for every activity, indicating the soil hazard. Scores may vary from 1 (very low risk) to 5 (very high risk), and include both the probability and the possible size of soil pollution. The final value of the Soil Immission Score depends on the soil protection level; the user has to select the appropriate package of precautionary measures. Soil protection may be achieved by either source-oriented provisions, aimed at minimizing the frequency of leakages, spills etc., or effect-oriented provisions, i.e. containment facilities to prevent the released materials to actually reach the soil.

Pollution Size Score

Only if the Soil Immission Score has a value of 2 ***and*** source- or effect-oriented provisions turn out not to be feasible (e.g. for economic reasons), the Pollution Size Score is determined. This score is a measure for the dimensions (i.e. the length) of the underground pollution plume and ranges from 1 (low) to 4 (high); if the value is 1, the activity is assessed a Soil Risk Score A*. This means that the activity is accepted under the condition that a monitoring programme is implemented. Furthermore, if any soil pollution is observed, soil sanitation is obligatory.

The Pollution Size Score depends on the soil chemical behaviour of the pollutant (mobility), the location typology (ground water flow rate, dimensions of the vadose zone) and the monitoring frequency. The source term (released quantity) is not included in this list. Dispersion calculations demonstrate that, although the source term does contribute to the concentration pattern in the underground, it is not the determining factor for the plume size.

Six location categories have been identified: polder, brook valley, elevated terrain, sandy areas with silt, clay or peat, idem without, and elevated sandy areas. The main features are the type (or absence) of infiltration and the groundwater flow rate. In the latter category, groundwater flow is not applicable, but the dispersion in the unsaturated zone is normative.

Soil Risk Assessment

The output of the BBB is the Soil Risk Category which is determined by combining the Soil Immission Score and the Pollution Size Score. which may be either A (low or negligible risk), A* (conditionally acceptable risk), B (elevated risk) or C (high risk). The ultimate aim is to achieve a soil protection level A for every individual installation. In case of a higher Soil Risk Score, additional precautionary measures are required.

Determination of the Soil Risk Category not only provides insight into the risks of individual installations, but also is a means for comparison of installations within a specific plant, industry or even a whole branche.

Current use of the BBB

The Decision Support System for Soil Protection has been implemented in the Netherlands and gains increasing support. Currently, several branche-specific systems have been or are being developed, specifying the activities from the different branches which significantly increases the method's user friendliness. Finally, TNO offer a computerised version of the Decision Support System called ASSISTERIX (Assessment of Industrial Site Terrestrial Risks).

REC: A decision support system for comparing soil remediation options based on Risk reduction, Environmental merit and Costs

Authors: M.H. Nijboer[1], J.P. Okx[1], E. Beinat[2], M.A. van Drunen[2] and R. Janssen[2].
[1] Tauw Milieu, P.O. Box 133, 7400 AC Deventer, The Netherlands (E-mail: mhn@tauw.nl).
[2] Institute for Environmental Studies, Boelelaan 1115, 1081 HV Amsterdam, The Netherlands.

Keywords: clean-up cost, cost-benefit analysis, decision support system, environmental impact, risk assessment

Problem definition

Soil remediation has often focused on a single perspective: reducing concentrations below given standards in the shortest possible time, so that a high soil quality can be restored. If standards are high enough, then the soil after remediation can be used for any purpose without restrictions. Although this is a very desirable outcome, experience has shown that this objective is difficult to achieve. Cost constraints and technical limitations make it difficult to restore a pristine soil in all situations. Clean-up management is first of all a matter of balancing out environmental achievements against reasonable costs

REC as a decision support system

Costs and benefits determine whether a remedial strategy is a feasible, effective and efficient solution. REC extends the traditional single perspective evaluation to a triple perspective by assessing the Risk reduction, Environmental merit and Costs of operations. Thus REC tries to give the decision-maker support for chosing the best remedial strategy at a site. REC provides a structure for the evaluation of different remedial strategies, REC intends to support rather than replace decision-makers .

Three perspectives

The REC methodology provides information about three aspects: Risk reduction, Environmental merit, and Costs. These three indices are assessed for each remedial alternative and are the basis for the comparison. The following figure shows, in a very simple fashion, the various activities which take place during remediation, their effects and their links with the objectives to be achieved. The thick-bordered boxes indicate which specific aspects are included in the R, E and C models. For instance, risk minimisation is the effects of reduced exposure. This, in turn, can be achieved by reducing the contamination at the site or by controlling the exposure path (e.g. by isolation).

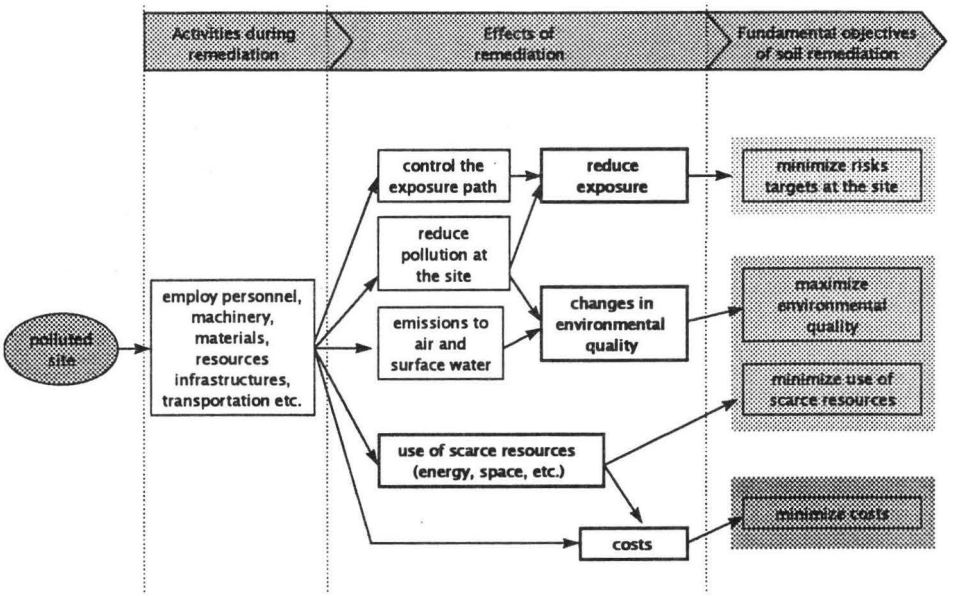


Figure 1 The viewpoints of taken by R, E and C.

Risk reduction gives the degree to which remedial action reduces risks for humans, ecosystems and other objects on the site. High risk reduction indicates that the residual risks after remediation are low.
Environmental merit gives the degree to which a remedial action achieves a positive environmental balance. Remediation alternatives could prevent the spreading of contamination and increase the stocks of clean soil and groundwater. However, they also use up resources, like energy, soil, (ground)water or space, and may pollute other media, like air or water. Environmental merit states the balance between environmental benefits and costs, so an integral environmental assessment is given. Costs give the total necessary costs for the clean-up of the site.
Costs include preparation, operation, maintenance and monitoring costs at all the phases of the operation. The calculation of costs makes it possible to include uncertainties.

REC in practice

REC has been tested and applied in real cases. It proves to be a useful tool for the analysis and evaluation of possible clean-up strategies for contaminated sites. Thereby REC gives a framework for the comparison of innovative clean-up strategies and more traditional alternatives. With REC it is possible to seek an optimal balance between Risk Reduction, Environmental merit and Costs, and to target the most effective and efficient clean-up alternative.

Reference

E. Beinat, M.A. van Drunen, R. Janssen, J.G.M. Koolenbrander, M.H. Nijboer, J.P. Okx en A.R. Schütte (alphabetic order) (1997) *The REC decision support system for comparing soil remediation options*, CUR/NOBIS, Gouda.

Confinement Techniques for Contaminated Topsoil

S.V.Mikheikin, A.N.Alekseev, L.V.Pronina, A.Yu.Smirnov
A.A.Bochvar Institute of Inorganic Materials (SRC RF VNIINM)
123060 P.O.Box 369 Moscow, Russia
E-mail: serge@bochvar.ru and 8910.g23@g23.relcom.ru

Key words: Contaminated soil, ecological effects, field experiment, in-situ treatment, protection, soil erosion, remediation.

Following the Chernobyl accident in 1986 over 2 mln. ha was exposed to radioactive contamination. Localities which had no vegetative cover generated radioactive dust. To suppress dust, the Bochvar Institute (VNIINM) in cooperation with the State Moscow University (MSU) have developed polymeric compositions based on new interpolyelectrolyte complexes (IPEC). IPECs result from interaction between oppositely charged polyions. The active polycationic groups interacting electrostatically with the kaolinite surface of negative charge. The negative charge can be caused by the partial dissociation of silanol groups Si-OH on the surface irregularities.

The homogeneous polymer solutions are easy to use and prepare industrially or in the field and suitable for application with standard special spraying equipment. Spraying with an aqueous polymeric solution (1-1.5 l/m) at a concentration of 2-4% produces in-situ a soil-polymer crust 3-5 mm thick, the largest share of the polymer being 3-4 wt.%. Because of its perfect water insolubility, the protective layer is of high resistance to fallout. The agglomeration of separate soil particles by polymers develops an increased resistance to erosion. For loose soils not stabilized by vegetative roots ($\rho_v \leq 1{,}20$ t/m^3), Eq.1 holds true:

$$V\,\Delta\, p_w = 1{,}55\sqrt{\frac{g}{\rho_o n'}\left[\left(1-\frac{P}{100}-\right)\bar{d}_w(\rho-\rho_o\ )\right]}, \quad (1)$$

Where $\mathbf{V}\,\Delta\,\mathbf{p_w}$ is the destructive speed for an initial soil humidity of w, m/s.; **g** - is the acceleration of gravity, m/s^2; ρ, ρ_o - are the density of solid phase and water, respectively, t/m^3; n' -is the factor describing the stream speed fluctuations (it is taken to be 2.3 for hillside streams); **P** - is the porosity of soil aggregates, %; $\bar{d}_w$ - is the weighted mean of the size of water stable aggregates, m;

It follows from Eq.1 that the destruction of larger aggregates requires a higher speed of streams. Light microscopy reveals that the protective layer entirely conserves the natural soil structure, precluding no gas- or moisture-exchange within topsoil. Depending on the nature and amount of a polymer, soil particles in stabilized soil-polymer layers can:

- stick together at the site of their contact. Interspaces are free for water and air;
- connect by long thin (~20 microns) bridges when particles of different size are separated by a considerable distance (from several microns to 1-2 mm);

- gluing together by thick polymer film when small-size particles (less 250 microns) attach themselves to larger ones (no less 700 microns). Thus, fine particles are picked up by the solution from interspaces between separate large particles, attracted and attached to them. It is the mechanism through which fine dispersed toxic matters are stabilized within a soil-polymer crust.

The polymers developed and related coats have been studied under laboratory and field conditions for soil remediation. Aerodynamic tests at 7-25 m/s show little mass transfer (0.01 g/cm s) for treated quartz sand and a mass transfer of 3.05 g/cm min for untreated sand at 10 m/s.

Properties of protective soil-polymer layer

Parameter	MM-1	MT-1
Confinement effeciency, %	as much as 98	as much as 98
Consumption, l/m^2	1.0	1.5
Thickness of the protective layer, mm	3-5	4-6
Mechanical strength, kg/cm^2	3-4	5
Life time, not less than, months	12	12
Resistance to fallout, mm	no less than 600	No less than 600
Toxicity LD/50, g/kg	44.98	-

Experience with eliminating consequences of the Chernobyl accident shows that the polymeric protective layer is necessary but inadequate for long-term preservation of contaminated surfaces. Combined application of the polymers and perennial seeds works well. During a year after treatment the layer protects soil and promotes vegetation. Prior to the polymer biodegradation the turf layer developed serves as a protector. A sowed-sprinkler prototype around a wheel tractor has been developed to make the best use of the soil treatment technique. Field experiment and in-situ treatment with new technique and sowed-sprinkler prototype realized with good results in 1986-90 in the Chernobyl area.

CONCLUSIONS.

1. Polymeric compounds based on interpolyelectrolyte complexes and a spraying technique have been developed for protecting contaminated soils against wind erosion;
2. Performance of the protective coats has been specified and compared with other polymeric compounds in laboratory and field conditions in the areas of Chernobyl NPP, of ecologically distressed of Aral Sea, and the Polyarny Ural;
3. The polymeric compounds developed are recommended for wide application in the event of industrial or ecological emergency.

ACKNOWLEDGMENTS

We are thankful to the Moscow State University team under the supervision of professor A.B.Zezin for their help in synthesizing IPECs.
The study is now financially supported by the International Science and Technology Center, Moscow (ISTC, Project # 589).

EFFECT OF MECHANICAL STRESS ON MICROBIAL SOIL REMEDIATION IN SOLID-STATE-BIOREACTORS

J. Scholz[1)], B. G. Müller[2)], J. Schwedes[1)], W.-D. Deckwer[2)]

[1)] Technical University of Braunschweig, Institute for Mechanical Process Engineering, Volkmaroder Str. 4/5, D - 38104 Braunschweig, Germany
[2)] GBF - National Research Centre for Biotechnology, Division Biochemical Engineering, Mascheroder Weg 1, D - 38124 Braunschweig, Germany

key words: availability, bioreactors, drums, homogenization, humic substances, hydrocarbons, microbiological degradation, organic compounds

INTRODUCTION

Solid-state-bioreactors are used in microbial soil remediation to enhance the degradation of hydrocarbon contaminants. This is achieved by moving the soil, leading to a sufficient oxygen supply of all soil compartments and to a homogenization of nutrients, contaminants and microorganisms in soil. This mixing helps to compensate the limitations of aerobic metabolism caused by lack of oxygen. An impairing of mixing and aeration by the formation of agglomerates of moist soil has to be prevented, therefore a mechanical stress is necessary in order to destruct the agglomerates mechanically.

RESULTS

A rotary drum reactor with grinding beads (ball mill) was used to study the influence of a mechanical stress on soil. The soil was treated at a moisture content slightly above the plastic limit but within the range of maximum microbial activity of about 50 % of field capacity. At this moisture content the soil shows plastic behaviour. This leads to a complete mixing of soil without comminution of soil particles and without disintegration of microorganisms. The mechanical stress shows several effects on the microbial activity and degradation of contaminants in soil:

- improved oxygen supply of microorganisms by the mixing
- compression of soil and therefore a decreasing oxygen supply in the time after the mechanical stress
- release of organic soil compounds into soil water
- improved availability of both nutrients and contaminants in soil

Furthermore the effects of the mechanical stress on the degradation of contaminants and microbial activity differ and depend on the kind, the duration and the intensity of the stress as well as on the concentration and the age of the contamination and the type of soil. The soil activity and the degradation of contaminants are not necessariliy correlated; an accelerated degradation of contaminants can be measured even if the oxygen consumption as an index for microbial activity does not change significantly. In Fig. 1 the oxygen consumption of mechanically stressed soils is shown after the mechanical stress. There is only a slight influence on oxygen consumption noticable after a period of about 9 days.

In spite of the almost similar oxygen consumption there are differences in the amounts of the degraded contaminats, i. e. hexadecane. Fig. 2 shows the measured degradation of hexadecane within 9 days after a mechanical stress in the rotary drum reactor with grinding beads. Additionally shown are the amounts of degraded hexadecane which can

be estimated by the assumption of complete mineralization to CO_2 (Eq. 1) and by the assumption of a simultanous formation of biomass and CO_2 in equal amounts of carbon (Eq. 2). An exclusive mineralization requires 24,5 mol oxygen per mol hexadecane. In case of equal generation of CO_2 and biomass only 15,1 mol O_2 are needed:

$$C_{16}H_{34} + 24{,}5\ O_2 \rightarrow 16\ CO_2 + 17\ H_2O \qquad \textbf{(Eq. 1)}$$

$$C_{16}H_{34} + 15{,}1\ O_2 \rightarrow 8\ CH_{1,7}O_{0,5} + 8\ CO_2 + 10{,}2\ H_2O \qquad \textbf{(Eq. 2)}$$

The total amount of consumted oxygen differs only slightly for all treatment times after 9 days for both alternatives of degradation. For short mechanical stresses the mass of degraded hexadecane corresponds to that estimated by Eq. 1 and Eq. 2. This is not the case for long treatment times t_b. The decrease of hexadecane cannot be explained by the consumption of oxygen alone. A possible reason is the increased fixing of contaminants in the humic substances in the soil caused by the release of soil organic compounds into soil water by the mechanical stress.

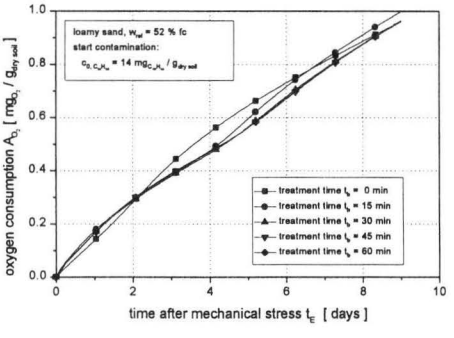


Fig. 1: Oxygen uptake of a contaminated soil after a once-through mechanical stress in a rotary drum reactor with grinding beads reactor with grinding beads

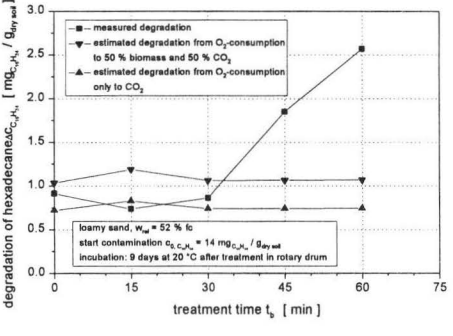


Fig. 2: Measured and from oxygen consumption estimated degradation of hexadecane after a once-through mechanical stress in a rotary drum

SUMMARY

A mechanical stress show effects on microbial soil activity and on degradation of contaminants. The whereabout of contaminants for long treatment times cannot be explained by the oxygen consumption. Even a once-through mechanical stress can lead to an accelerated degradation. A further increasing can be realized by using a continous or periodic stress. In all cases a compression of the soil has to be considered which leads to a worse oxygen supply and therefore to lower microbial activity.

These studies are funded by the Deutsche Forschungsgemeinschaft (DFG) in the scope of the research group "Biological Processes with disperse solids".

FEASIBILITY OF DECONTAMINATION OF LEAD-POLLUTED SOIL BY AQUEOUS SODIUM CHLORIDE AND SODIUM HUMATE SOLUTIONS

Esma Tütem, Reşat Apak, Kubilay Güçlü and Jülide Hızal

Department of Chemistry, Faculty of Engineering, University of İstanbul, Avcılar, 34850, İstanbul, Turkey

Keywords: Lead, soil, decontamination, leaching, sodium chloride, sodium humate.

Heavy metals accumulated in soils may be harmful to soil and its boundary ecosystems pusing environmental risks to human health. An excess of heavy metals adversely affects the biological activity of soil organisms. Elevated heavy metal content reduces yields of food and fodder crops or increases concentrations of pollutants in plants. Clean-up and decontamination of heavy metal polluted sites is essential for preventing surface water and groundwater pollution, too.

To eliminate hazards of heavy metal contaminated soil, various remediation techniques have been developed which are based on either immobilization of metal within soil or removal of metal from the soil matrix. Chemical leaching is associated with metal removal. The chemicals used for this purpose are acids (e.g., H_2SO_4, HCl, HNO_3, acetic acid)[1-4], bases (e.g., NaOH)[1] and chelating agents (e.g., EDTA[5,6], diethylenetriamine[1], citric acid[5], NTA[7].

In this study, the capability of NaCl as the neutral salt solution to complex exchangeable lead(II) —in the form of Pb(II)-Cl complexes— and of sodium humate naturally occurring in soil to chelate lead have been investigated as regards to determining their potential benefits in Pb removal from soil.

Five hundred mg samples of two different soil types (characteristics shown in Table 1) were agitated with 25 mL of 25 ppm lead(II) —as $Pb(NO_3)_2$— solution for 6 h at 25 °C using a thermostatic shaker/water bath. The lead-saturated soil samples were separated by centrifugation, washed with distilled water, and equilibrated with either pure water, 0.01-0.40 M NaCl solution or 0.05-0.20% (w/v) sodium humate solution under identical conditions as used for metal retention. The determination of lead in the filtrate was made by AAS using a Varian SpectrAA 220 FS model instrument.

The results of leaching tests as described above carried out for 1.16 mg/g Pb-loaded soil samples are depicted in Table 2. The desorption percentage for lead(II) with water was negligible confirming irreversible uptake.

Contaminated Soil '98, Thomas Telford, London, 1998, 1179–1180

Table 1. Characteristics of soil samples

Sample no.	pH	sand, %	powder, %	clay, %
1	7.0	63	11	26
2	6.5	85	4	11

Table 2. The leaching efficiency, % of lead-loaded soil samples with complexing solutions (Pb content of sample: 1.16 mg/g soil)

	Complexing Solution						
	NaCl (M)				Na-humate (%, w/v)		
Sample no.	0.01	0.1	0.2	0.4	0.05	0.2	0.5
1	28.3	97.8	97.5	97.8	42.2	52.5	81.7
2	26.6	76.0	85.0	88.3	47.0	55.3	84.8

The leaching efficiencies for Pb(II) shown in Table 2 reveal that both complexing agents, i.e., NaCl and Na-humate, are capable of ≥80 % Pb removal over a definite concentration limit. These findings are in accord with the literature data reporting the lead mobilizing effect of deicing-salt mixtures (i.e., NaCl + $CaCl_2$) applied on heavily iced railroads in the winter, the plausible mechanism being ion exchange and chloro-complex formation[8]. A dilute (~0.2 M) NaCl solution proved to be a simple and inexpensive agent for leaching out exchangeable lead from the soil matrix in the form of chloro-complexes.

REFERENCES

1. Palmer, J. P., Williams, K. P. and Prosser, H. J. (1995) Decontamination of metal-containing soils, in W. J. van den Brink *et al.* (eds.) Contaminated Soil'95, Kluwer Academic Publishers, Dordrecht, pp. 883-893.
2. Khan, S., Nandan, D. and Khan, N. N. (1982) The mobility of some heavy metals through Indian red soil, *Environ. Pollut. (Series B)* **4**, 119-125.
3. Rulkens, W. H., Assink, J. W. and van Gemert, W. J. (1985) *Contaminated Soil*, Plenum Press, New York.
4. Thöming, J. and Calmano, W. (1995) Remediation of heavy metal contaminated soils by acid leaching and electrolytic metal separation, in W. J. van den Brink *et al.* (eds.) Contaminated Soil'95, Kluwer Academic Publishers, Dordrecht, pp. 895-902.
5. Hui, C., Qiaoju, Z. and Jian, Q. (1992) Cleanup of Cd-polluted soil using chelating agents, in M. A.Usmen and Y. B. Acar (eds.) Environmental Geotechnology, Balkema, Rotterdam, pp. 365-368.
6. Barona, A. and Romero, F. (1996) Fractionation of lead in soils and its enfluence on the extractive cleaning with EDTA, *Environ. Technol.*, **17**, 63-70.
7. Elliot, H. A. and Brown, G. A. (1989) Comparative evaluation of NTA and EDTA for extractive decontamination of Pb-polluted soils, *Water, Air and Soil Pollution*, **45**, 361-369.
8. Bauske, B. and Goetz, D. (1993) Effects of deicing-salts on heavy metal mobility, *Acta Hydrochim. Hydrobiol.*, **21**, 38-42.

CENTRIFUGE MODELLING OF SELF-WEIGHT OF CONTAMINATED OR PARTIALLY CONTAMINATED DREDGED SLUDGES

D. Levacher[1], F. Marot[1,2], P. Conil[2], M. Boutouil[1]

1. *Groupe de Recherche en Génie Civil, GRGC, Université du Havre, B.P. 265, 76055 Le Havre, France*
2. *Bureau de Recherches en Géologie Minière, BRGM, B.P. 6009, 45060 Orléans 2*

Key words : dredged material, simulation model, disposal sites, sludges

SUMMARY :
Most of dredged sludges are devoted to sea deposits. Disposal at sea are carried out in conformity with the environment agreements. Following the contamination attached to the muds, disposals at sea become forbidden. So, deposits are performed near the shore or on ground in previous controlled storage areas. The use of partially or not contaminated dredged materials as landfarms or embankments is conducted with the study of self weight consolidation. The proposed study is concerning the feasibility of self weight consolidation tests by centrifuge modelling. This experimental way is well adapted to study the behaviour of the disposals of dredged sludges (Balay et al.) and mainly to predict the settlements in the cases of reuse of these storage areas.

INTRODUCTION :

Disposals at sea are submitted to restrictive conditions so as to protect the marine environment against heavy metals, chemical or organic matters pollution. These contaminants are usually contained in the dredged sludges which are characterized by fine sediments (clays, silts, fine sands). Often, the dredged sludges are used to fill storage areas in near shore or in land to create industrial platforms, coastal zones, gardened embankments, landfarms.... Tentatively this is made in assessing the pollution risks. An other way is to consider the dredged sludges as partially contaminated waste materials. To enhance the value of a such waste material is a priority. An assessment for treating (decontamination, stabilization, solidification) sludges may be first studied after mineral, chemical and mechanical characterization (Boutouil et al.). Heavy metals decontamination techniques for estuarine and canal dredged sludges have been studied (Marot). The decontamination processes make that the treated sludge is shared in a granular and a fine sediment. One of possible uses of these decontaminated sludges is the landsfarming or the filling of quarries, of embankment industrial areas... To study the land disposal behaviour during only the consolidation, an experimental work have been carried out on centrifuge models. The consolidation phenomena has been observed on a canal sludge before and after subjecting the heavy metal decontamination.

THE DEPOSIT MODELLING :

The model is chosen to be representative of a natural deposit as a set of compartments in a landfarm. It is characterized by a small height of 2.5 m spreading over many hectares. The seepage conditions are offered by the surface and by the bottom recovered by a geotextile layer. So, six consolidation cells are used to simulate the large and thin natural deposit. Each cell (diameter 300 mm, height 200 mm, wall thickness 6 mm) is installed in the centrifuge container (long 1200 mm, large 800 mm, height 360 mm).

The series of tests are concerning a canal contaminated canal sludge corresponding to different natures : virgin (B), decontaminated with a fine (F) and a granular (G) parts (figure 1). Two deposits models are the same samples among the six samples (nature of sludges, seepage conditions, settlement transducers). A couple of cells for F and G distribution so as to appreciate the dispersion on the obtained results. In the case of B virgin sludge, one is drained on two faces (B2) and the other only by the surface (B1). In order to evaluate the scale effect, two series of consolidation tests are run out at 50 g and 70 g levels. All the identification and physical parameters are determined at the beginning of series of tests and at the end of centrifugation at 1 g level completed by the measurement of undrained shear strength. Some consolidation parameters of two series of centrifuge tests are given in table 1.

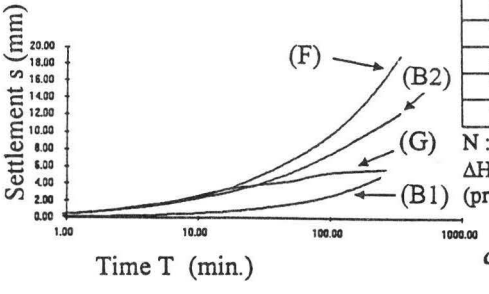


Figure 1 : Settlement (s).time (T) curve (model data)

N (g)	$\Delta H/H_0$ (%)	$\Delta H_\infty/H_0$ (%)	T (days
50	36.4	43.1	525
50	35.0	42.2	525
70	34.4	44.2	525
50	36.0	42.2	583
70	35.3	44.2	583
70	39.6	44.2	926

N : gravity ratio, ΔH : settlement, H_0 : initial height ΔH_∞ : final settlement (Asaoka method), T : time (prototype data)

Table 1 : Comparative results of the consolidation of the virgin sludge (B2)

CONCLUSIONS :

Centrifuge modelling offers to the environmental engineers, a possibility to study the consolidation of a dredged sludge disposal in land and to design the storage areas and their reuse for landfarming. The reproducibility of tests has been checked, using some samples (2 here) for each series of tests of consolidation, whatever the distribution size of the sludge. Comparing the results of the two series of tests, at 50 et 70 g, validation of scale effects is also checked.

REFERENCES :

Balay J., Berdat R. and Harfouche L (1988) Etude en centrifugeuse de la consolidation sous poids propre de sols très lâches, *Centrifuge 88*, Corté Ed., pp. 193-200

Boutouil M., Levacher D., Marot F., Conil P., Sanson P. and Troalen J.P. (1997) Devenir des vases et boues de dragage : solidification et stabilisation, *Symposium Internat. Géologie de l'Ingénieur et Environnement*, AIGI, Athènes, pp. 1635-1642

Marot F. (1997) Caractérisation et traitement de sédiments de dragage contenant des polluants métalliques et des matières organiques, *Thèse de doctorat de l'Université du Havre*, 184 p.

SOIL VAPOR EXTRACTION: TEST AND CONTROL

Jörg Johannsen[1], Ekkehard Petzold[2], AndreasThimm[1]

1 Dipl.Chem. Ing. Jörg Johannsen, Dipl. Chem. Andreas Thimm, Johannsen & Thimm - Environmental Consult, Ostkirchstr. 56, D 44269 Dortmund
2 Dr. rer.nat. Ekkehard Petzold, Sachverständigenbüro / Dr. Petzold Consult, Weissenburgstr. 14, D 48151 Münster

Key words: Aromatic hydrocarbons, halogenated hydrocarbons, volatile organic compounds (VOC), soil vapor extraction, test values, soil contamination

SUMMARY
The removal of VOC using soil vapor extraction is mostly not described sufficiently because of missing basic data. Some of the parameters which should be determined to get a detailed data base are presented.

KURZFASSUNG
Die Sanierung von Schäden durch VOC mittels Bodenluftabsaugung wird oft durch das Fehlen von Randbedingungen nicht ausreichend ausgelegt. Einige Daten, die vor Beginn einer Maßnahme zu ermitteln sind, werden vorgestellt.

RÉSUMÉ
Souvent on ne peut pas décrire suffisament l'assainissement des dommages par VOC avec l'aspiration de l'air de terre pour raison de la manque de tous les paramêtres. Quelque-uns des paramêtres que doivent être déterminés pour obtenir un resultat exact sont présentés.

1. The Problem: Missing essential data

Underground contaminations with volatile organic compounds (VOC) can be remediated very well by soil vapor extraction, especially when soil porosity is high to permit a sufficient air flow, which applies for instance to sand or gravel.

Before starting a soil vapor remediation project, it is necessary to perform vapor extraction tests. These tests give informations about soil porosity and the amount of VOC which have to be removed and neutralized.

Boode describes (Contam. Soil '95, pp. 799) tests resp. mathematical models before starting a big soil vapor extraction project.

From our point of view, it is always - especially on small or less contaminated sites - necessary to perform these tests to define the exact size and the best fitting equipment for soil vapor extraction. In detail this means:
- Small volumes of soil vapor samples during the investigations do not give informations about the intensity of the soil vapor contamination resp. the amount of VOCs in the ground.

- If the samples show high values of VOCs in soil vapor this does not necessarily mean that they can be extracted easily, especially from loam or clay.
- High initial values can decrease rapidly and shortly after beginn of soil vapor testing: In this case there might be no real need for remediation.

These informations can not be obtained by regular soil vapor sampling, when pumping only small air volumes with only little reduced pressure. The different physical conditions of this sampling method will lead to incorrect conclusions.

2. Data collection: Test and Control

Some marginal conditions for a better performance are:

- A continuous control of the air flow referring to the technical equipment that is used gives useful hints for the expected further progress in remediation.
- Parameters worth to be controlled continuously are for instance: Contents of Oxygen and CO_2, temperature, pressure, humidity of soil air, explosibility (at petrol stations e.g.), air flow.
- Sampling for laboratory analyses should be made under defined and reproduceable conditions.
- An continuous control of the main contaminant(s), using a IR or GC device with data storage, combined with analysis in a laboratory gives hints for a suitable analytical on-site method that can be performed automatically.
- The soil vapor extraction test should be carried out for various soil depths, depending on the geology on the site. The use of packers is essential in this case.
- The radius of influence has to be investigated in order to get the correct amount and position of remediation wells.
- All informations should be saved on data loggers or computers.

The composition and concentration of the contaminants fixes the method of cleaning the soil air before emitting. Using active carbon filters it has to be found out if the suitable active carbon has been used during the soil air extraction test. The ratio between the costs for active carbon and the adsorbance capacity can often be optimized by using special carbon types. In some cases like adsorption of vinyl chloride a special adsorption technique and carbon is needed anyway.

When using other cleaning methods like thermal combustion (e.g. for high concentrations of hydrocarbons) -which are usually high in costs- a preparatory test is necessary to avoid wrong -and expensive- decisions.

A continuous control of the above mentioned parameters during the remediation test phase will also give a better chance to optimize and scale up the future operation. Especially treating cohesive soils (loam, clay) an intermitting operation will yield the same results as a continuous operation, but it saves a lot of energy. Finally a good data base gives the chance to shorten remediation time, and, additionally, a good documentation of the remediation process for the authorities and/or those who pay the expenses.

REMEDIATION OF GROUNDWATER AND AQUIFER MATERIAL AT THE RHO OIL REFINERY, WITH PARTICULAR REFERENCE TO THE USE OF *EX SITU* BIOREMEDIATION

J Turrell[1], L Clark[1], P. Berbenni[2] and F. Nobili[3]

[1] WRc plc, Henley Road, Marlow, Bucks, SL7 2HD, England.
[2] Polytechnic di Milano, Piazza Leonardo da Vinci, 32-20133, Milan, Italy
[3] Geochem srl, 20122 Milan - Via Santa Sofia, 27, Italy

Key words: aromatic hydrocarbon contamination, biodegradation, remediation

Summary
A problem encountered by the oil industry throughout the world is the remediation of groundwater and aquifers beneath closed Refineries and Oil Terminals. The Rho Refinery, in Milan covers an area of more than 1 200 000 m^2 and is located on heterogeneous alluvial materials. Chemical analyses have shown pollution of the shallow materials to be widespread and variable with depth. On-site bioremediation is an accepted technique for the removal of hydrocarbons from contaminated soil or aquifer material. However, the conditions under which bioremediation is undertaken vary with the type of soil or aquifer material and with the type of hydrocarbon pollutant. Laboratory experiments were undertaken at the WRc laboratories in England to determine the optimum condition for biorestoration of aquifer material beneath the refinery. The test results show that on-site bioremediation using biopile technology under controlled conditions is a feasible method for soil and aquifer material clean-up at the Rho.

Background
Remediation technology is developing extremely rapidly in response to demands generated by the present environmentally conscious regulatory agencies. The Rho Refinery in Italy is currently the subject of a phased programme of clean-up. The distribution of both heavy and light hydrocarbon contaminants suggest that the site remediation will need two solutions:

- In-situ remediation for the deep pollution (4 m-15 m depth) (Not covered by this poster).
- The shallow aquifer and soil pollution will be dealt with by on-site technologies and this poster describes tests undertaken to optimise those technologies.

Values of Total Petroleum Hydrocarbons in the shallow soil exceed 3000 mg kg^{-1} in a few cases, but most are less than 100 mg kg^{-1}. A relatively common method used for the remediation of soils or unconsolidated aquifer materials is the biodegradation of hydrocarbons under aerobic on-site conditions in structures known as 'biopiles'. The conditions needed for the remediation however, will vary from site to site according to the material being remediated and the hydrocarbon being degraded. Laboratory experiments were therefore undertaken at the WRc to determine the optimum condition for biorestoration of aquifer material beneath the refinery.

Experimental Conditions

The most effective biodegradation or remediation will take place when a number of factors are optimised: the microbiological biomass, the concentration of hydrocarbons in the material, the temperature, the water content, the oxygen content, and the nutrient content. A work programme was designed using small laboratory bioreactors to determine the optimum conditions for bioremediation in a closely controlled environment. It was intended that these optimum conditions then could be used to operate field scale remediation biopiles. Agip Petroli owners of the refinery provided two large samples of aquifer material that had been polluted by heavy and light oils respectively, to ensure optimisation of the degradation conditions for a range of different hydrocarbons. Each type was subjected to variable conditions in two banks of ten temperature-controlled 55 kg bioreactors (see Figure 1).

Figure 1 A schematic diagram of the bioreactors

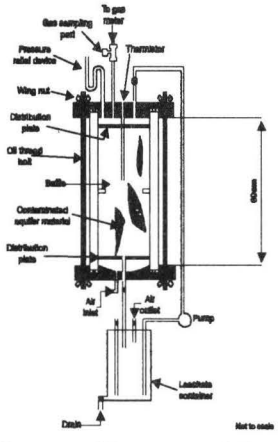
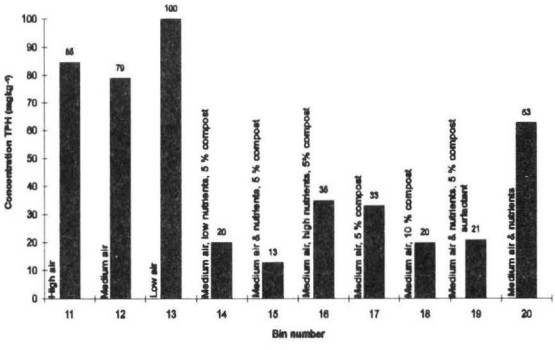


Figure 2 Hydrocarbon concentrations at 16 weeks, Bins 11 to 20, normalised to Bin 13



The aquifer materials were homogenised and analysed by GCMS (Gas Chromatographic Mass Spectrometry), to establish hydrocarbon concentrations before treatment. Sub-samples of each aquifer material were then mixed with the relevant additives and again homogenised. Following all additions, the bioreactors were sealed and the airflow rates and temperature controls adjusted to meet the experimental criteria. The water capacity of the material supplied by AGIP was 60%, and from previous studies this represents the optimum level for biodegradation.

Results and Conclusions

Significant losses in hydrocarbons occurred in both the light and heavy contaminated material over the sixteen week test period, Figure 2 illustrates losses in the material contaminated with heavy oils. A large percentage of both the aliphatic and aromatic components of the hydrocarbons was removed by volatilisation and biodegradation in the first eight weeks of remediation. The most effective combination of treatment parameters was shown to comprise an air flow of approximately 40 m^3 air per hour, nutrient addition at levels used in standard composting and the addition of a mature compost at 5% by weight. The results show that on-site bioremediation using biopile technology under controlled conditions is a feasible method for soil and aquifer material clean-up at the Rho Refinery, and that ideal temperatures for remediation would be obtained within the summer period without the need for additional heating.

LABORATORY AND FIELD PILOT EVALUATION OF CO-METABOLIC BIOVENTING FOR THE REMEDIATION OF SOIL CONTAMINATED WITH TRICHLOROETHENE (TCE) AND TRICHLOROETHANE (TCA)

P. Morgan[1], G.D. Sayles[2], L. E. Moser[3], D.J. Gannon[3], D.H. Kampbell[4], T. Franz[5], C.M Vogel[6], D.W. Major[7], M.J. Bell[8] and M.W. Holmes[1]

[1] ICI Technology, P.O. Box 8, Runcorn, WA7 4QD, UK.
[2] US Environmental Protection Agency, National Risk Management Research Laboratory, Cincinnati, OH 45268, USA.
[3] Zeneca Corp., Sheridan Park Environmental Laboratory, 2101 Hadwen Road, Mississauga, Ontario, L5K 2L3, Canada.
[4] US Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, P.O. Box 1198, Ada, OK 74820, USA.
[5] Beatty Franz & Associates, 18 King Street East, Bolton, Ontario, L7E 1E8, Canada.
[6] US Air Force, AFRL/MLQE, 139 Barnes Drive, Suite 2, Tyndall AFB, FL 32403-5323, USA.
[7] Beak Technologies Inc., 42 Arrow Road, Guelph, Ontario, N1K 1S6, Canada.
[8] ICI Chemicals & Polymers Ltd., P.O. Box 13, Runcorn, WA7 4QF, UK.

Keywords: bioremediation, case history, chlorinated hydrocarbons, contaminated soil, field test, halogenated hydrocarbons, in-situ bioremediation, soil clean-up, trichloroethylene, vadose zone

INTRODUCTION

This poster describes the laboratory evaluation and field testing of trichloroethene (TCE), dichloroethene (DCE) and 1,1,1-trichloroethane (TCA) remediation in vadose soil by co-metabolic bioventing with oxygen and growth substrate(s) supplied in the gas-phase. The project was undertaken at Dover Air Force Base (AFB), Delaware, USA by the Remediation Technologies Development Forum (RTDF) Bioremediation of Chlorinated Solvents Consortium.

SITE DESCRIPTION

The site selected for the demonstration project was adjacent to a jet engine maintenance building (Building 719). Soil properties and contaminant concentrations are summarised in Table 1.

Soil fraction	wt%	Parameter	Value	Contaminant	Max. value
Gravel	3	pH	8.0	TCE	5 mg/kg
Sand	55	TKN	220 mg/kg	cis-1,2-DCE	18 mg/kg
Silt	29	Total phosphate	36 mg/kg	1,1,1-TCA	150 mg/kg
Clay	13	TOC	<0.5%	Xylene	14 mg/kg

Table 1. Composition, properties and contaminant concentrations in soil at co-metabolic bioventing test area. TKN = total Kjeldahl nitrogen; TOC = total organic carbon.

LABORATORY EVALUATION OF CO-METABOLIC BIOVENTING POTENTIAL

Microcosm studies demonstrated that stable biodegradation of chlorinated solvents could be supported at significant rates (up to 19 mg TCE/kg soil.year) by toluene and propane. Biodegradation supported by methane was short-lived and decreased rapidly with time. Butane did not support biodegradation. Addition of nitrogen and phosphorus did not enhance activity and no toxic effects occurred at the contaminant concentrations present.

Continuous flow column experiments (14 kg soil) were then undertaken using toluene and propane as primary substrates. Pulse feeding was found to give optimum balance between performance and field operability. Both substrates gave effective and stable degradation of the contaminants but propane was selected for field application because of the degradation rate supported (approximately 9 mg TCE/kg soil.year; 400 mg TCA/kg soil.year), the relatively low high molar requirement of propane (27 mol propane/mol TCE degraded) and ease of use in the field.

FIELD PILOT TEST UNIT

The field pilot test unit is illustrated schematically in Figure 1 and operates with automated pulse injection of propane and air. Routine monitoring of soil gas composition (O_2, CO_2, propane, TCE, TCA) and soil temperature is backed up by an intensive sampling and analysis programme at the start and shut-down of operation to determine contaminant mass balance and changes in microbial population. Preliminary operating data will be presented and related to development of a 3-dimensional mathematical computer model of co-metabolic bioventing.

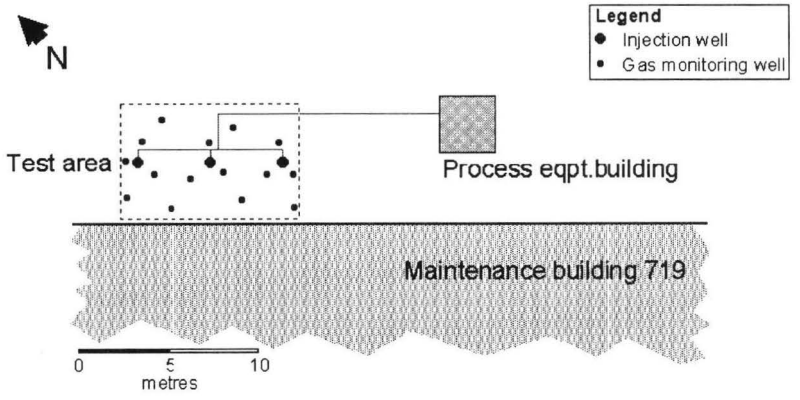


Figure 1. Schematic layout of co-metabolic bioventing test cell at Dover AFB.

DEVELOPMENT OF A BIOREACTOR PROCESS FOR TREATMENT OF PAH CONTAMINATED SOILS

T. Sobisch, H. Niebelschütz*
L.U.M. GmbH, Rudower Chaussee 5, D-12489 Berlin, Germany
**ARGUS GmbH, Reuchlinstraße 10/11, D-10553 Berlin, Germany*

keywords: bioavailability, bioreactors, chemical oxidation, clean-up technologies, extraction, fine particles, gasworks, PAH, physico-chemical processing, washing stage

Bioremediation, often a very economical option for soil decontamination, has restricted applicability for soils contaminated with polycyclic aromatic hydrocarbons (PAH´s).
In a series of experiments with soil samples of contaminated sites we investigated different options for a combined physicochemical and biological treatment process.
Contaminant concentration was characterized either by HPLC (16 individual PAH compounds according to the EPA 610 Priority Pollutant list) or by UV-derivative spectrometry (pyrene). Additives used were all of technical grad. Surfactant combinations designed to enhance bioavailability (Sobisch et al. 1998) T10 and T36S are mixtures of a hydrophilic and a hydrophobic component. Other additives (nonionic and anionic surfactants, dispersants, polymeric compounds) were also tested during the investigations (extraction of soils with surfactant solutions, effect of washing pretreatment, biodegradation studies).
A feasibility study for extraction of soil samples with surfactant solutions revealed that even with surfactant combinations with very pronounced extraction efficieny associated surfactant costs will be high or a sophisticated procedure for surfactant recycling will be necessary. Therefore, implementation of a process with preextraction of the contaminated material will not be economically feasible.
Biodegradation could be enhanced by addition of special surfactant combinations and other additives (Sobisch et al. 1998) or by a washing pretreatment of the soil.

A sandy soil of a former gaswork site had been investigated in more detail. The initial PAH concentration was 1086 mg/kg (340 mg/kg pyrene). The content of organic material / low density particles was very low, however, soil grains were covered with a film of mineral oil (total petroleum hydrocarbons according to DEV H-18 1000 mg/kg).
The sample was further characterized by wet-sieving after a washing treatment in a laboratory attrition cell. The fraction of soil fines < 63 µm was small (approx. 5 %) and had a substantially higher load of PAH, however, treatment by simple soil washing does not seem promising because a PAH concentration of 470 mg/kg was measured for the "cleaned" sand fraction. Addition of a dispersant, which was effective in soil washing of soils with considerable organic matter content (Sobisch et al. 1995, 1996), caused only a small improvement of cleaning efficiency. Addition of 0.5 % of a surfactant combination (per soil) with high extraction efficiency resulted in a further contaminant reduction of 15 %. The best results were obtained by adding 0.5 % of a hydrophobic cosolvent and 0.1 % of a dispersant simultaneously (220 mg/kg PAH).
Influence of washing pretreatment on biodegradation in slurry tests was investigated shaking 20 g nonsterilized soil with 180 ml mineral salt solution for 10 days. The washing pretreatment seriously enhanced bioavailabilty, even when performed without additves. Whereas for the original soil sample the PAH load reduced to 500 mg/kg, the residual

concentration for the sample washed previously with water alone was 146 mg/kg. For the sample washed with addition of cosolvent and dispersant there was only a minor further improvement (residual PAH 113 mg/kg).
In another set of experiments the influence of different surfactant combinations and dispersants on contaminant removal during biodegradation slurry tests was investigated (conditions same as above). Addition of surfactant combinations enhanced contaminant reduction, however addition of the dispersant was more effective and required only very low concentrations. Adding 0.5 % T10 per soil PAH load reduced to 365 mg/kg, whereas addition of 0.01 % of Z2 resulted in a residual concentration of 250 mg/kg.
However, even under improved conditions biodegradation was to slow to obtain low enough residual values in resonable times. Therefore a new two stage bioreactor system was developed (patent pending).

The new bioreactor system consists of a reactor for simultaneous biological and wet processing of soil and of a filled column. A slurry of suspended soil fines and particles of low density is continuously transfered to the column filled with a granular material of high sorption capacity, which removes fine particles and contaminants and can be regenerated by back flushing. After passing the column the suspension is recirculated.
The new system proved to be very effective. Whereas after a week in previous slurry biodegradation tests the pyrene load of the sandy soil only reduced to 275 mg/kg, it could be reduced to 6 mg/kg using a laboratory system, which consisted of a stirred reactor, a pump and a column filled with granular activated carbon. Optimization could be achieved by addition of surfactant combinations or by addition of a polymeric additive, which supports biofilm formation (Z18). Thus during 3 days pyrene load was reduced to 12 mg/kg (0.5 % T36S) or to 10 mg/kg (0.1 % Z18). With preceding incubation of the soil with nutrients the latter value could be reduced further to 4 mg/kg.
The treatment procedure could be also adapted to a fraction of soil fines from a soil washing plant. In this case an oxidative pretreatment, addition of a dispersant and of surfactant was necessary for an effective decontamination.
The system described does not require replacement of the column filling. During experiments using the same column (more than 35 times) so far efficiency of the system did not reduced.

References

Sobisch, T., Kühnemund, L., Hübner, H., Reinisch, G. and Olesch, T. (1995) Investigations on enhanced washing of tar contaminated soils, in W.J. van den Brink et al. (eds.) *Contaminated Soil'95* Kluwer Academic Publishers, pp. 1357 - 1358

Sobisch, T., Hübner, H., Kühnemund, L. and Olesch, T. (1996) Auswahl von Additiven zur Erhöhung der Reinigungswirkung von Verfahren zur Behandlung Teer- und PAK-verunreinigter Böden, in NORDAC (ed.) *NORDAC Schriftenreihe Band 5* Economica Verlag, Bonn, pp. 88 - 97

Sobisch, T., Heß, H., Niebelschütz, H. and Schmidt U. (1998) Effect of additives on biodegradation of PAH in soils, *Colloids and Surfaces A, IAP97 Special issue*, in press

Acknowledgement

We greatfully acknowledge the support of the Bundesministerium für Bildung, Forschung und Technologie under grant numbers FKV 0211001J6 and FKV 015042J6.

Regional Effectiveness of Contaminated Site Remediation Activities

R. C. Schwarzenbach[1], A. Heitzer[1], B. Stäubli[2] and R. W. Scholz[1],

[1]Chair of Environmental Science, Natural and Social Sciences Interface ETH Zürich, ETH Zentrum HCS, CH-8092 Zürich, Switzerland,

[2] Amt für Abfall, Wasser, Energie und Luft, Walchetor, CH-8090 Zürich, Switzerland

Key words: contaminated soil administration, environmental management, mass transport calculation, petroleum hydrocarbons, soil clean-up

The main clean-up objective for contaminated sites is the elimination or reduction of actual or potential hazards. At construction sites contaminated materials are often excavated and subjected to off-site treatment or reuse depending on the quality of the materials. In consequence, these materials are distributed within a region according to the selected treatment. For a specific contaminated site the clean-up objectives may be achieved locally but from a regional perspective it remains unclear how the contaminated materials are distributed and if they cause a new pollution problem.

In order to assess the overall effectiveness of contaminated site remediation it is necessary to extend the boundaries of the system considered beyond the local site to a regional level. Focusing on material and pollutant fluxes which result from treatment activities the fate of materials and pollutants can be analysed and quantified in space and time. Such information is important for both, the regional management of contaminated sites and for the planning of local clean-up actions in particular.

Using the method of substance flow analysis, the waste material fluxes resulting from the excavation and treatment of contaminated sites have been investigated. As a first step, the total amount of waste produced in the Canton of Zurich, a state in northern Switzerland, was compared to the amount of waste resulting from off-site treatment activities in the same region. The total amount waste materials produced in the Canton of Zürich was 6.3 million tons in 1995 including domestic waste, construction and demolition waste and industrial waste materials. For the same year the contaminated soil material from off-site remediation projects accounted for about 1 to 2 percent of the total waste produced. However, this same material contributed to arround 30 percent of the annual amount of hazardous waste produced in the same region. This comparison demonstrates that the main problem is the quality of the materials and not the amount of material.

In order to address the question of the whereabouts of the materials and the contaminants in more detail 73 closed remediation projects were analysed with respect to material and pollutant fluxes. All projects considered were located in a particular region of the Canton of Zurich called Limmat valley. The material was predominantly contaminated with petroleum hydrocarbons. For the analysis a model was developed taking all the relevant processes and fluxes into account (see figure 1). Material from contaminated sites was subjected to off-site treatment, transferred to landfills or directly reused as "clean soil". In the region considered the available treatment technologies included bioremediation, soil washing or thermal treatment in a cement kiln. Alternatively, material could be exported out of the system considered mainly into other landfills. The figure includes four different types of landfills.

These are defined by federal law and differ in their quality requirements for the deposited materials.

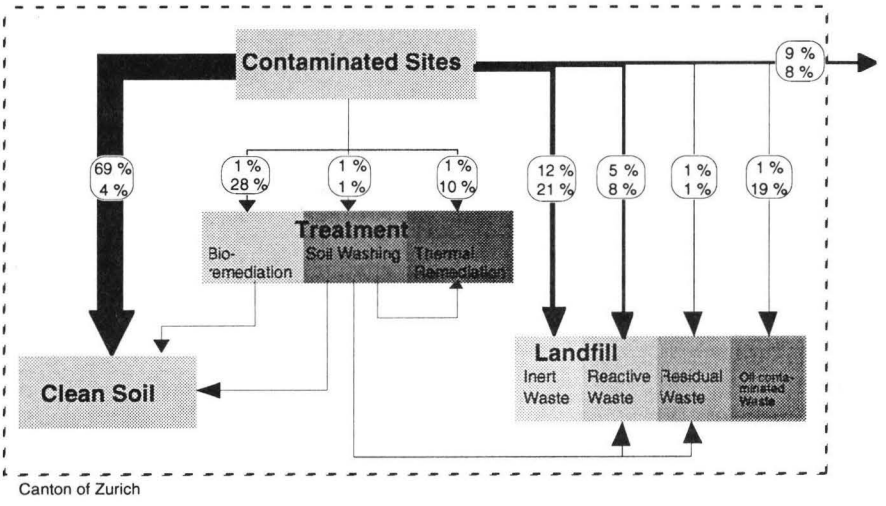


Figure 1: Massflux and petroleum hydrocarbon flux of waste materials from contaminated site remediation projects from 1991 to 1993 in the Limmat valley. Arrow thickness is proportional to mass fluxes.

The most important process for the material distribution within a region is the identification of contaminated materials and the assignment of waste materials from a contaminated site to a disposal or treatment path. Figure1 shows the mass- and petroleum hydrocarbon pollutant fluxes for the years 1991 to 1993.

Most of the excavated material at contaminated sites could be reused as clean soil material. About 19 percent of the contaminated materials were deposited on landfills in the years 1991 through 1993. Only a small mass fraction was subjected to treatment. Focusing on the contaminants, the picture looks different. About 39 percent of all petroleum hydrocarbons were extracted in the treatment process, 49 percent were deposited on landfills and only 4 percent were transferred with the large massflux to the process clean soil. These data demonstrate that most of the hydrocarbons were effectively controlled by the governmental ordinances and guidelines on the classification of contaminated materials.

A temporal analysis of the relative material fluxes revealed a significant change in treatment practice from disposal on landfills towards decontamination of excavated material. Whereas between 1991 and 1993 49 percent of the hydrocarbons were transferred into landfills this number has decreased to 11 percent for the period of 1994 to 1996. This can be largely attributed to the implementation and availability of new treatment technologies as well as to new state regulations. A new stationary soil washing plant started operations in 1993 and new state regulation became effective in 1993 and 1996.

At the regional scale, the analysis of substance fluxes resulting from materials contaminated with hydrocarbons revealed a very effective prevention of uncontrolled distribution of pollutants. Hence, the systematic analysis of the regional cleanup activities and the quantification of the relevant substance fluxes can provide an important contribution to the evaluation, planning and management of contaminated site treatment from an overall or governmental perspective.

DECISION SUPPORT SYSTEM FOR TREATMENT OF DREDGED SEDIMENTS

J. Joziasse[1], T. Bakker[2], P.G. Eggels[1]

[1] TNO Institute of Environmental Sciences, Energy Research and Process Innovation, P.O. Box 342, 7300 AH Apeldoorn, The Netherlands
[2] RIZA Institute for Inland Water Management and Waste Water Treatment, P.O. Box 17, 8200 AA Lelystad, The Netherlands

Keywords: dredged material, sediments, treatment methods, environmental effects, costs, decision support system, life cycle assessment, computer model

SUMMARY
A decision support system for treatment of dredged sediments (DSTS) has been constructed, in which the environmental effects of various treatment options applied can be compared. The effects are evaluated by scores on environmental themes like global warming and acidification, using life cycle assessment methodology.

INTRODUCTION
Millions of tons of less or more polluted sediments are being dredged in the Netherlands annually. These dredgings result from routine maintenance of waterways for shipping and water supply, as well as from remediation of polluted sediment sites. Until recently the only outlet for this polluted material was dumping in storage depots. As a result of several research programmes that have been completed over the last decade, a number of separation and cleaning techniques have become available for treatment of polluted sediments.
Different water authorities, charged with responsibility for dredging activities, have to decide how to handle the dredged material. In order to make the right decisions and to take into account new treatment methods, the authorities and their advisors require information concerning possibilities and impossibilities of specific treatment methods in the given situation, and concerning the environmental effects of these treatment methods. The 'Decision Support system for Treatment of dredged Sediments' (DSTS) aims to present the information required.

SYSTEM DESCRIPTION
Based on a flexible database filled with information on the different individual treatment techniques, the DSTS judges which chains of techniques can be applied for the specific dredged material under question. First, a number of potentially applicable chains are selected. Next, each chain is analysed in order to predict the composition of the different resulting products and to quantify the expected environmental effects and the amount of waste. The quantification of the effects is accomplished by the use of the 'LCA" (Life Cycle Assessment) methodology. The use of scarce commodities, emissions, etc. for the various processes is converted into scores on a limited number of environmental themes, like global warming, acidification, smog formation, etc. Next, the scores are normalised using the total volume of the issue under consideration in the Netherlands. Optionally (using more or less subjective weight factors) the scores can be combined into a single number as an indication of the environmental sacrifices.

Contaminated Soil '98, Thomas Telford, London, 1998, 1193–1194

OUTPUT

The output is presented in tabular and graphical form. An example of a so-called

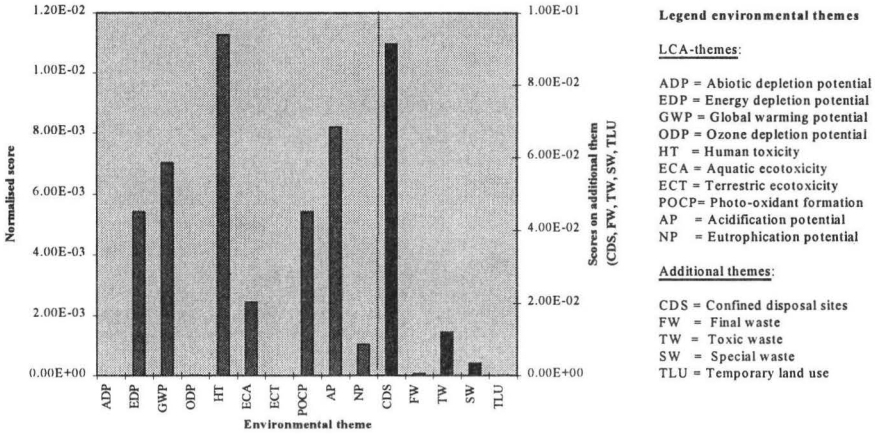


Figure 1 Environmental profile (fictive case)

'environmental effects profile' for a fictive case is presented in figure 1. This figure shows the normalised scores on the environmental themes considered.
Comparison of the output for different treatment options provides information that can assist the water authorities in making decisions. The rough cost figures, that are presented in the output as well, can assist in serving this purpose. Limiting conditions based on legislation and physical and environmental planning, however, are not part of the DSTS.

PROSPECTS

The DSTS is available as a prototype for testing at present. New treatment techniques and new chains of techniques can be added to the system database and technique information can be changed, based on recent research results or practical experience. With this new information predictions will become more and more reliable.
Preliminary tests have proven the potential of DSTS as a useful tool within the field of sediment management. Nevertheless, more techniques and further details concerning the treatment techniques already incorporated have to be added to the database, before the system can be presented as a tool to be used more widely. For the next decade limitations in possibilities for sediment storage in depots will urge the water authorities to search even more for alternative solutions to handle the removed polluted sediments. Based on this expectation, the further development of the DSTS should take place in close co-operation with the intended users.
One of the challenges to be met is the development of a consistent and reliable method for the assessment of environmental effects of in-situ sediment (before and after dredging), in order to visualise also the benefits of a dredging operation. By offering this option the system will be suited for use in prioritisation of sites to be remediated. In order to achieve this, risk analysis methods will have to be combined with the LCA-methodology for the assessment of the environmental effects.

THE TREATMENT OF AQUIFERS CONTAMINATED WITH ARSENIC, ZINC AND CADMIUM BY THE BIPOLAR ELECTROLYSIS TECHNIQUE: THE OVERPELT PROJECT.

Stany Pensaert

SOILS NV, Haven 1025, Scheldedijk 30, B-2070 Zwijndrecht, Belgium.

Key words: groundwater treatment, heavy metals, arsenic, zinc, cadmium, mercury, aquifer.

INTRODUCTION: THE PROBLEM AND THE SOLUTION

In the summer of 1997 SOILS NV started a large groundwater remediation project in the north of Belgium, where many heavy metal black spots are concentrated, due to former metallurgical activities.

In this particular case, the remediation of deep aquifers is necessary, as these are contaminated with zinc, arsenic, and to a lesser extent cadmium.

The remediation follows a pump-and-treat technique, with the treated water to be discharged in the public sewer system. This imposes to the treatment technology treatment target levels of 300, 50 and 10 µg/l for respectively zinc, arsenic and cadmium.

Standard water treatment techniques can hardly reach these levels at a reasonable cost. For this reason the new, in-house developped bipolar electrolysis technology of SOILS NV has been introduced.
This technology is principally based on the attraction of the heavy metal ions towards one of the electrodes, and the electrochemical mediation of the solution in order to control pH and potential to the required levels. All heavy metals are transformed in insoluble compounds (hydroxides, carbonates or other) which are removed in a second consecutive step of decantation and filtration.
No chemicals are used; electrical current is the only 'additive', which makes the technique good controllable and safe for operation.

THE OVERPELT PROJECT.

The Overpelt project has been divided into two phases. The first, preparative step of the remediation programme was a large scale pilot test, completed in December 1997. For this purpose SOILS NV designed a 25 m^3/hr mobile plant consisting of 9 containers, which will be later implemented in other groundwater remediation projects.

Contaminated Soil '98, Thomas Telford, London, 1998, 1195–1196

The aim of this preliminary test phase is threefold. Firstly the efficiency of the bipolar electrolysis technique on this specific polluted groundwater was to be studied. Secondly all upscaling problems had to be evaluated and solved, in order to design and complete succesfully the actual treatment plant with a required capacity of 250 m^3/hr. Thirdly a BATNEEC study had to be performed, in order to evaluate the costs and yield of the process.

RESULTS.

As for the efficiency, the results exceeded the expectations. The aquifer groundwater concentrations which originally showed levels of 7.5 mg/l for zinc, 0.6 mg/l for arsenic, and 32 µg/l for cadmium, were reduced easily below the above mentioned standards. Effluent concentrations of 214, 13 and 3 µg/l were obtained for respectively zinc, arsenic and cadmium.

All upscaling problems have been studied and solved. This will set the basis for the design of the treatment plant to construct in 1998.

In the BATNEEC-study, in which treatment efficiency and running cost are compared, it was shown that the mentioned treatment results can be attained at a running cost of about 0.5 US$ per m^3 of water. Depreciation costs of the equipment are in the same order, such that a total operational cost of 1 US$/$m^3$ can be maintained.
The Bipolar Electrolysis technology fully meets the BATNEEC requirements.

AQUIFER REMEDIATION.

The next project phase, to be carried out in 1998, will be the design and construction of an electrochemical treatment plant with a hydraulic capacity of 250 m^3 per hour, which will be operational for a predicted remediation period of 60 years. The plant will be operational in Spring 1999.

This treatment plant will be the largest application of electrolysis in environmental technology at the moment.

SOILS NV was awarded the European Better Environment Award for Industry in 1996 for its Bipolar Electrolysis.

SOILS NV, Haven 1025, Scheldedijk 30, B-2070 Zwijndrecht, Belgium.
Tel: +32 3 250 55 11 Fax: + 32 3 250 52 54
E-mail: pensaert_stany@dredging.com

THE USE OF METHYLENE UREA AS NITROGEN FERTILIZER IN OIL-WASTE LANDFARMING

Peltola, R [1]; Turpeinen, R [2]; Koivunen, M [3]; Kähkönen, L [3] Salkinoja-Salonen, M [1]; Romantschuk, M [4]

[1] Dept. of Applied Chemistry and Microbiology and [4] Dept. of Biosciences, P.O. BOX 56, FIN-00014 University of Helsinki [2] University of Helsinki, Dept. of Ecological and Environmental Sciences, Niemenkatu 73 FIN-15210 Lahti; [3] Kemira Agro Oy, P.O. BOX 44 FIN-02271 Espoo;

Keywords: bioremediation, oil products, nitrogen, microbial activities

Landfarming is a biological method to treat oil waste, especially oily sludges. For good results, nitrogen must be added to the soil. Nitrogen can be added in the form of urea or ammonium. Due to urease and nitrification activities in soil, urea is transformed to metabolites which evaporate and leach from the soil. Methylene urea, (MU, urea formaldehyde) is a low soluble source of nitrogen. In this research we used MU as a fertilizer at an oil-waste landfarming site and studied its effect on bacterial populations and activities in the soil.

The test field chosen was divided into seven sections. Samples were taken prior to addition of different amounts of MU or urea to six of the sections. The control section remained untreated. Six replicate samples were taken from each section 17 and 70 days after nitrogen additions. The pH, nitrification potential, plate count of heterotrophic bacteria, and oil concentration were measured.

The nitrification potential in each section is shown in figure 1. The potential increased rapidly after the addition of nitrogen except in section 5, where no increase was observed. With addition of ca. 1000 kg N ha^{-1} urea had roughly a two-fold effect on the nitrification potential: nitrification potential was double in section where urea was used, compared to section where equal amount of MU was used.

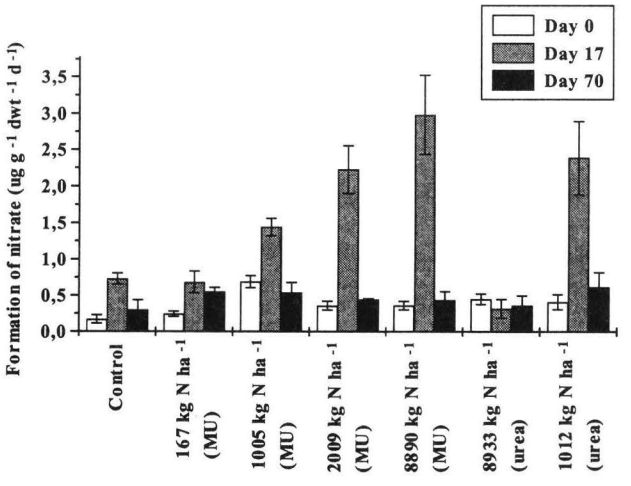


Figure 1: Nitrification potentials in test sections.

Bacterial numbers in the soil remained almost constant except in section 5, where the number of colony forming units was dramatically decreased (figure 2).

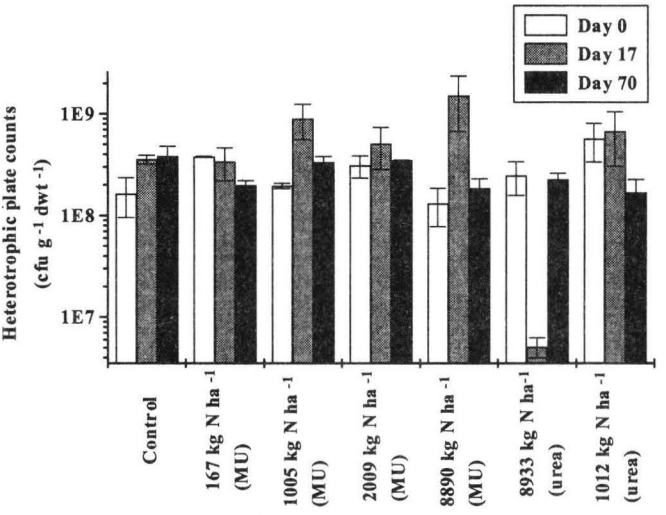


Figure 2: Plate counts of heterotrophic bacteria from test sections.

The pH remained close to neutral during the observed time period except in section 5, where at day 17 the pH had increased to 8.6. This increase was apparently caused by accumulation of ammonia. The toxic effect of this accumulation can be seen in figures 1 and 2: the nitrification potential was not increased and the number of heterotrophic bacteria was dramatically decreased.

For the upholding of high population densities of oil degrading heterotrophic bacteria, MU is a better choice as a nitrogen fertilizer than urea. MU did not induce nitrifying bacteria as much as urea did. Furthermore, the effect of MU on soil pH is much smaller than the effect of urea. It is expected that the nitrogen concentration stays optimal for longer times using MU, offering more constant conditions for oil degrading bacteria thus improving the oil degrading efficiency in the landfarming process.

References

Alef, K. (1995). Nitrogen mineralization is soils, in K. Alef and P. Nannipieri (eds.) Methods in applied soil microbiology and biochemistry. Academic Press, London, pp. 234 - 245.

REMEDIATION OF TETRACHLOROETHENE-CONTAMINATED GROUNDWATER AT A SITE IN NORTHERN ENGLAND

J. Blackmore

WRc plc, Henley Road, Medmenham, Marlow, Buckinghamshire, SL7 2HD, UK

Key words: Groundwater remediation, chlorinated hydrocarbons, soil vapour extraction

Introduction

In 1993, the owners of a textile factory in north-east England were successfully prosecuted by the National Rivers Authority (NRA) under Section 85 of the Water Resources Act, following a groundwater pollution incident involving the chlorinated solvent tetrachloroethene (PCE). WRc were subsequently appointed by the factory owners to design and undertake a programme of site investigation and remediation to tackle the contamination. A phased project was undertaken, leading to the implementation of a remediation scheme comprising hydraulic control of groundwater migration, soil vapour extraction and point of use treatment of the groundwater supply at a nearby Maltings.

Background

The PCE contamination originated from 2 sources: a spillage from a tanker in 1992, and long-term disposal of contaminated water to a soakaway which only came to light following the spill. The factory is located on approximately 12 m of glacial deposits, referred to here as the shallow aquifer, overlying a formation of alternating sandstones and mudstones. The sandstone units of the latter are locally important for public and industrial water supplies; sampling by the NRA identified contamination of the groundwater supply to a Maltings some 300 m from the textile factory. No other sources were affected, but a clear source, pathway and target had been identified, with concentrations at the Maltings' source substantially in excess of the limit of 10 $\mu g\ l^{-1}$. As soon as PCE had been detected in the Maltings' source, by the NRA's preliminary investigations, a GAC plant was installed to effect point-of-use treatment.

WRc's programme of site investigations established the presence of very high concentrations of PCE (over 150,000 $\mu g\ l^{-1}$) in the shallow groundwater in the area where the spill occurred and close to the soakaway. In these two areas, high concentrations of PCE were also detected throughout the depth of the drift deposits in disturbed samples taken during percussion drilling of the boreholes.

Remediation Scheme

Details of the three main elements of the remediation scheme which was implemented at this site are given below:

1. A soil vapour extraction system, centred on the two contamination hot-spots, comprising 46 boreholes at various depths into the unsaturated zone. This system began operating in February 1995, and to date has removed an estimated 12,000 kg of PCE; the client's original estimate of PCE losses was some 2 orders of magnitude less than this figure. PCE levels have been reduced to close to background levels, and agreement has now been reached with the Environment Agency (successor body to the NRA) to de-commission this part of the system.
2. Boreholes were drilled in each of the hot-spot areas, principally to effect hydraulic containment. The groundwater was initially treated in an air stripping tower prior to Consented discharge to foul sewer, but WRc have now helped to obtain an Abstraction License from the Environment Agency, meaning the treated groundwater will be available for non-potable use in the factory. This will result in annual savings of some £30,000 from reduced mains water and effluent discharge fees, as well as providing an incentive to maintain the hydraulic control system. The 2 boreholes have so far removed approximately 600 kg of the solvent, whist PCE concentrations have been reduced to around 6,000 $\mu g\ l^{-1}$ (Figure 1).
3. The GAC plant at the Maltings continues to provide the only cost-effective solution to the contamination of the deep sandstone aquifer units. This plant will be required for a considerable period, but the treatment effected on the shallow aquifer should ensure that the timescale is of the order of years rather than centuries (12,000 kg of PCE could have raised the concentration of the annual licensed abstraction rate at the Maltings to 10 $\mu g\ l^{-1}$ for 2,200 years). An estimated 180 kg of PCE has been removed by the GAC plant.

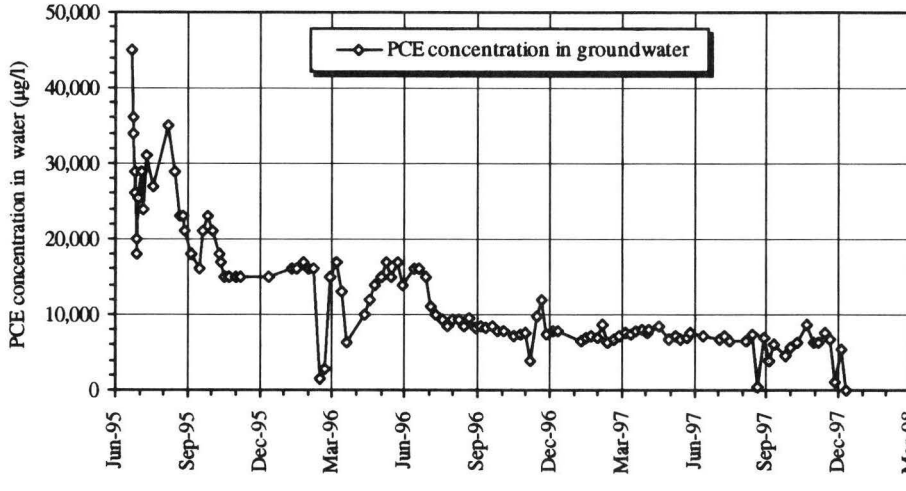


Figure 1 Concentration of tetrachloroethene in shallow groundwater during remediation

IN SITU IMMOBILIZATION OF HEAVY METALS IN CONTAMINATED SOILS: EFFECTS ON PLANTS AND EARTHWORMS.

L.A. Oste, T.J. Schröder, S. Bakker, M. Oppenheimer and Th.M. Lexmond.

Wageningen Agricultural University, Dept. of Environmental Sciences, Sub-dept. of Soil Science and Plant Nutrition, P.O.Box 8005, 6700 EC Wageningen, The Netherlands. E-mail: leonard.oste@bodhyg.benp.wau.nl

Keywords: bioassays, cadmium, ecotoxicological, immobilization, in-situ treatment, metal, plants, quality of the soil, sorption, zinc

INTRODUCTION

Soil quality assessment should take into account potential toxic effects of contaminants on plants, animals and human beings. The free metal concentration in the soil solution is considered to be a key factor in determining the toxicity of heavy metals to flora and fauna and, therefore, deserves a central position in assessing soil quality. The free metal concentration is influenced by the total quantity of metals in the soil, the number of binding sites in the solid phase and environmental conditions, notably pH and redox status. The quality of a contaminated soil can not only be improved by removing the contaminant, but also by reducing the metal concentration in the soil solution.

A decrease in the dissolved metal concentration can be achieved by adding metal binding chemicals to the soil. Immobilization is a non-destructive *in situ* technique, suitable for large areas and relatively cheap. The latter depends, of course, on the price of the additive.

EXPERIMENTAL

Binding agents and deionized water were mixed through the soil and the mixture was stored in polyethylene bags in the dark. After 4 weeks the experiment started. To evaluate the immobilizing effect we used three methods: the extractable metal concentration with 0.01 M $CaCl_2$ in a 1:10 (w/v) ratio, the uptake of cadmium and zinc into the edible parts of Swiss chard (*Beta vulgaris* var. *cicla*) and the accumulation into the tissue of earthworms (*Dendrobaena veneta*). For all experiments we used two sandy soils from a zinc smelter affected area in the North of Belgium (table 1).

Table 1: Soil characteristics.

	%C	% clay	pH-$CaCl_2$	Cd aqua regia (mg/kg)	Zn aqua regia (mg/kg)
soil A	2.2	7.0	5.2	2.5	211
soil B	2.0	2.0	5.0	9.6	437

We investigated the effect of two immobilizing agents: beringite and δ-manganese oxide (also called birnessite). Beringite is a modified alumino silicate originating from the fluidized-bed burning of coal mining refuse (Vangronsveld et al., 1996). δ-MnO_2 was made in our laboratory. This substance has a high affinity for metal ions, due to a

large negative surface charge at common soil pH values and a large surface area (McKenzie, 1981).

In experiment 1 we investigated the effect of δ-MnO_2 on the accumulation by Swiss chard. We added δ-MnO_2 to soil B at six different levels (replicated 3 times) varying from 0 to 16 g/kg.

In experiment 2 we compared beringite and lime. We treated soil A with beringite (0, 12.5, 25, 50 and 100 g/kg) and $Ca(OH)_2$ (0, 0.5, 1, 2, and 4 g/kg). We also included two levels of δ-MnO_2 (12.5 and 25 g/kg). In experiment 1 and 2 plants were grown in 2.5 l pots in a greenhouse and harvested after six weeks.

In experiment 3 beringite (0, 25, 50 and 75 g/kg) and δ-MnO_2 (6.25, 12.5, 18.75 and 25 g/kg) were added to soil B. Twelve earthworms, obtained from a vermiculturist, were put into each jar. After a 3-week period, collected worms were kept in petri dishes for 3 days to empty their gut and analysed.

RESULTS

Experiment 1 showed δ-MnO_2 to be a strong immobilizing agent. The concentration of Cd and Zn in $CaCl_2$ as well as the tissue concentration in plants decreased by approximately 90% at the highest δ-MnO_2 level compared to the untreated soil.

In the second experiment doses of beringite and lime were chosen so as to achieve the same pH range. Figure 1 shows that we succeeded in doing so. Beringite did not affect plant uptake more than liming, while the δ-MnO_2 data are clearly lower at the same pH. This also holds for the metal concentration in 0.01 M $CaCl_2$.

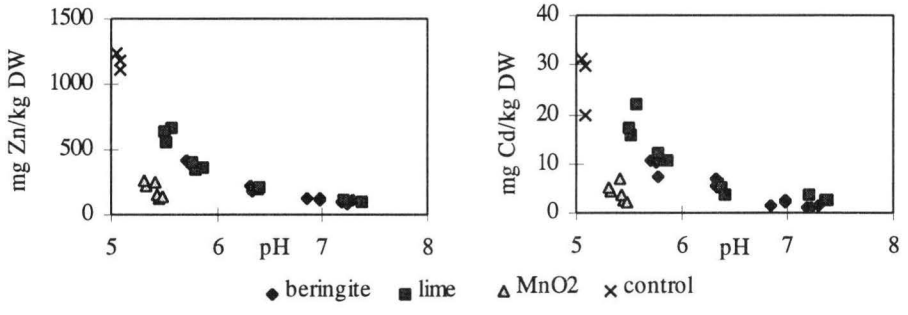


Fig. 1: Zn (a) and Cd (b) concentration of Swiss chard related to pH (exp.2).

Although application of immobilizing agents strongly affected the $CaCl_2$-extractable metal concentration and plant uptake, it did not influence the concentration i worm tissue at all. Evaluation of the effectiveness of immobilizing agents apparently depends on the criteria used.

REFERENCES

McKenzie, R.M. (1981) The surface charge on manganese dioxides. *Aust. J. Soil Res. 19, 41-50.*

Vangronsveld, J., Colpaert, J.V. and Van Tichelen, K.K. (1996) Reclamation of a bare industrial area contaminated by non-ferrous metals: physico-chemical and biological evaluation of the durability of soil treatment and revegetation, *Environ. Poll. 94, 131-140.*

Directed microbial manipulation in an artificial groundwater/sand aquifer system using an electrical current.

Dearlove, J.P.L.[1], Abbott, A.[1], and Rigby, C.[2]

[1] Westlakes Scientific Consulting Ltd, The Princess Royal Building, Westlakes Research Institute, Moor Row, Cumbria, UK. CA24 3LN

[2] University of Leeds, Department of Earth Science.

Key words: In-situ groundwater remediation; micro-organisms; barriers; remediation concept.

SUMMARY

Experimental work has shown that the micro-organism *B. subtilis* 168 may be removed from an artificial groundwater solution by an electrical current emitted by either an inert carbon or a non-inert Fe(III) electrode, surrounded by a simulated sand aquifer medium. These preliminary results provide tentative support for the concept of creating *in-situ* biofilm barriers on aquifer substrates to remediate contaminated groundwater.

INTRODUCTION AND REMEDIATION CONCEPT

Current research has established that micro-organisms associated with a biofilm at a liquid:solid interface appear to exhibit the greatest metabolic activity. Microbes may more effectively bind metals as part of a biofilm, rather than if they remain in a planktonic condition or reversibly adhered to a surface. Aqueous interfaces may initially satisfy microbial nutritional requirements, or an emergent biofilm may establish an enhanced nutrient adsorption system. Surface nutrient concentrations appear to become increasingly important in low nutrient environments such as those found in most natural groundwater systems (Marshall, 1988).

If micro-organisms are to be utilised in the treatment of low nutrient contaminated groundwaters, it would appear that the development of a biofilm provides a more favourable and stable environment. If groundwater is to be treated, the biofilm needs to be established on the aquifer substrate perpendicular to the direction of groundwater flow. A method is thus required so that naturally occuring or introduced micro-organisms can be influenced to establish a biofilm at a predetermined location.

This paper describes initial results of experiments designed to explore the possibility of developing a method for directed microbial manipulation in a geomatrix of acid-washed sand using an electrical field to create a viable biofilm. Previous work has tended to concentrate on the prevention of biofouling through electrode-induced repulsion, not the use of electrodes to attract micro-organisms. The purpose of these laboratory tests are to determine the viability of attracting the micro-organism *B. subtilis* 168 towards an anodic electrode and to remove the micro-organism from the aqueous phase. Bacterial populations may undergo directed migration in response to an applied chemical gradient (chemotaxis) (Mercer *et al.*, 1993). Electrode choice is thus potentially important in terms of initiating chemotactic migration. Inert and non-inert electrodes were compared to determine if any observed migration occurred as a result of chemotaxis and not from the application of an electrical current.

EXPERIMENTAL PROCEDURE

A parent culture of *B. subtilis* 168 was used in all inoculations. Stationary phase cultures were used in all experiments and were grown overnight in BDH Standard II

nutrient broth, in an incubator shaker at 37°C. The composition of the artificial groundwater was as per the low ionic-strength eluent of Fontes *et al.* (1991). Sand aquifer geomatrix surrounding the anode was simulated using a nylon gauze sheath (approximately 30x100mm) filled with approximately 50 grams of 0.1 to 0.3mm acid-washed sand sterilised by autoclave at 121°C for 15minutes. Sterilised inert carbon or non-inert Fe(III) electrodes (approximately 5x100mm) were placed centrally within the sand-filled sheath. The sand sheath/electrode system was placed in a lidded polypropylene basin (300x150x100mm) filled with sterilised artificial groundwater inoculated with 200ml of broth culture. A current of 20mA and 40mA was applied to the inert and non-inert electrodes respectively. Duplicate reference systems with no power supply were used as experimental controls. 1ml samples were removed from the inoculated artificial groundwater at intervals of 30, 60 120 and 240 minutes. An additional 1ml sample was taken at a 1 minute interval for the inert electrode during repeat experiments. Viable counts on the solution samples were obtained from serially-diluted agar plate counts, incubated overnight at 37°C. Triplicate samples and single samples collected contemporaneously from different points within the experimental system were collected to evaluate analytical accuracy and system bias.

SUMMARY OF RESULTS AND DISCUSSION

Space does not permit a full tabulated description of the experimental results. The following discussion summarises the more pertinent features.

A significant proportion (approximately 90%) of *B. subtilis* 168 was removed from a low ionic-strength artificial groundwater by both the inert carbon and non-inert Fe(III) electrode systems described. Cell removal from the aqueous phase appears to be complete within 30 minutes, with no significant increase or decrease in viable cell counts up to removal of the current after 240 minutes. Only a small increase appears to occur after 1 minute although further work is required. Transfer of viable *B. subtilis* 168 from the sand/anode system back into the artificial groundwater was not observed.

Comparison of the results for the inert carbon and Fe(III) electrodes appear to indicate that electrode choice does not significantly affect the size of population removed from the aqueous phase. However a marked colour change in the sand surrounding the Fe(III) electrode from colourless to brown/red indicates a localised chemical gradient generated by cathode dissolution and precipitation around the anode. This may have an impact on the solution ionic strength and practical applications of the technique.

CONCLUSION AND FURTHER WORK

The aim of this work, to determine the viability of attracting the micro-organism *B. subtilis* 168 towards an anodic electrode and to remove the micro-organism from the aqueous phase, has been achieved. Further studies are now required to determine the development of a viable biofilm on the aquifer geomatrix surrounding the electrode and to assess the performance of this biofilm as a passive contaminant migration barrier in a simulated groundwater flow environment.

REFERENCES

Fontes, D., Mills, A., Hornberger, G., and Herman, J. (1991) Physical and chemical factors influencing transport of microorganisms through porous media. *Applied and environmental microbiology*, **57**, 2473-2481.

Marshall, K (1988) Adhesion and growth of bacteria at surfaces in oligotrophic habits. *Canadian Journal of Microbiology*, **34**, 503-506.

Mercer, J., Ford, R., Stitz, J., and Bradbeer, C. (1993) Growth rate effects on fundamental transport properties of bacterial populations. *Biotechnology and bioengineering*, **42**, 1277-1286.

LOW COST INCINERATION RESIDUES DETOXIFICATION PROCESS.

P.H. Lee, V. Nasserzadeh, J. Swithenbank;[1] C. McLeod;[2] J. Goodfellow.[3]

[1]Sheffield University Waste Incineration Centre (SUWIC), Department of Chemical & Process Engineering, University of Sheffield, Mappin Street, Sheffield S1 3JD , UK.

[2]Centre for Analytical Science (CAS), University of Sheffield, Dainton Building, Brook Hill S3 7HF, UK.

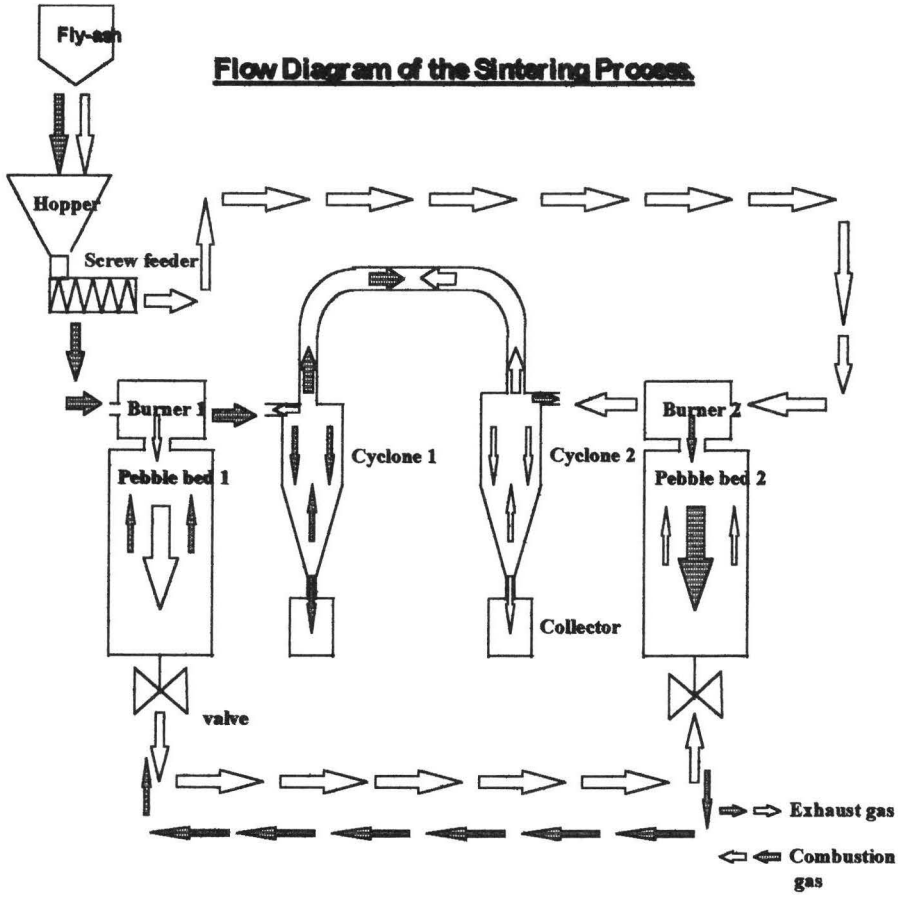
[3]Dyson-Hotwork Engineering Limited, Dewsbury WF12 9DB, UK.

Keywords: Thermal treatment, PCDD/Fs, incineration, environmental impact, hazardous waste, heavy metals, fixation, costs, decontamination techniques.

SUMMARY

The aim of this research work is to develop a novel, cheap and efficient technology capable of transforming toxic fly ash from waste incineration industries into an inert material. The stable material produced is intended to be used in construction or buildings industries. The total toxic fly ash generated in the UK is already reached 100,000 tonnes/year from municipal waste incinerators alone and is expected to increase by a significant amount in the future. A low cost decontamination process based on the application of a regenerative heating concept is investigated. The regenerators are a pair of pebble beds which provide preheated air to the burner up to 85% of the process temperature. The toxic ash is introduced as the hot combustion gas enters a cyclone. The ash particles having a fine size of less than 300 μm are heated to the sintering temperature in the fraction of a second during which the particles reside in the cyclone. The particles are then separated from the gas and collected by centrifugal force. At the same time the gas is drawn through the second pebble bed where its heat content is recovered. The

sintering of these fly ash particles results in the destruction of its toxic organic components as well as fixation of its heavy metal content to form an unleachable material. The results obtained from this study are expected to have a major impact on the future codes of practice and standards dealing with toxic fly ash. Thus, the hazardous residues which is now being landfilled at a high cost can either be used safely or be landfilled at a much lower cost.



POTENTIAL USE OF β-CYLODEXTRIN FOR BIOREMEDIATION OF CONTAMINATED SOIL

Molnár, M.[2], Gruiz, K[2], Fenyvesi, É.[1] and Szőnyi, M.[2]

[1] Cyclolab Ltd., 1117 Budapest, Dombóvári út 4-6, HUNGARY
[2] Technical University of Budapest, Department of Agricultural Chemical Technology, 1111 Budapest, Gellért Sq. 4. HUNGARY

Keywords: bioremediation; oil contaminated soil; β-cylodextrin; cyclodextrin complexation; soil toxicity; contact biotest

The biodegradation of hydrocarbons in the soil is a complex process, whose quantitative and qualitative aspects depend also on the bioavailability and the toxic effect of the contaminants (1).
Cyclodextrins (CD) are typical „host" molecules and due to their favourable structural character form inclusion complexes with a wide variety of organic compounds. This kind of „molecular encapsulation" may affect on bioavailability of the contaminants during biodegradation and also modify toxicity on soil microbes, plants and animals.
Large scale laboratory experiments (40 kg) were carried out for bioremediation of soils contaminated by transformer oil. The influence of randomly methylated β-cylodextrin (RAMEB) on the biodegradation process and on the toxic effect of contaminated soil was investigated by chemical and biological analyses in details. Biodegradation process was followed by both soil and soil-gas analyses. Degradation rate of the contaminant and the microbial activity was followed by measuring the oil content and the cell concentration of the soil. The CO_2 and O_2 content of the soil-gas was measured continuously during the bioremediation. The oil composition was analysed by capillary GC and FTIR.
The effect of RAMEB on soil ecosystem and on soil toxicity was investigated by bioassays. Direct contact biotests were used to simulate the interaction between contaminants and testorganisms. Organisms of three different trophic level were applied as testorganisms. Direct contact test method were developed and used (2, 3, 4).

- bacterial : *Photobacterium phosphoreum* bioluminescence inhibition test,
- plants : *Sinapis alba*, *Lepidum sativum* germination and root elongation test,
- animal : *Folsomia candida* mortality test (4).

The use of the ß-cyclodextrin during bioremediation of hydrocarbon-contaminated soil resulted in three different effects.
1. Enhanced the biodegradation of oily contaminant in case of Diesel-oil, transformer oil and PAHs. By forming a complex with CD hydrocarbons presumably desorbed from fine soil particles and are made available to microorganisms.
2. Decreased the toxicity of the hydrocarbon contaminants. This retard effect of the cyclodextrin is due to the characteristics of the formed complex. After encapsulation the partition of the contaminant between solid- and water phase has been changed; a more advantageous equilibrium concentration is connected with an increased desorption.
3. Increased the availability of many of the nutrients of the soil resulting in higher activity and production. This effect may be measured also in case of uncontaminated soil.
The molar ratio of β-cylodextrin and the contaminant showed an optimum.
In the following tables and figures we demonstrate the characteristic changes measured by the testorganisms of three trophic levels.

Table 1. *Sinapis alba* root - and shoot - elongation test

Soil	4 month bioremediation				8 month bioremediation			
	$ED20_{root}$ [g soil]	$ED50_{root}$ [g soil]	$ED20_{shoot}$ [g soil]	$ED50_{shoot}$ [g soil]	$ED20_{root}$ [g soil]	$ED50_{root}$ [g soil]	$ED20_{shoot}$ [g soil]	$ED20_{shoot}$ [g soil]
Contaminated	1.2	< 0.625	4.0	0.8	1.7	< 0.625	4.8	1.2
Cont. + 0.5 % CD	1.6	< 0.625	4.2	1.1	1.8	< 0.625	6.4	1.8
Cont. + 1.0 %CD	3.4	0.8	10.0	2.8	3.4	< 0.625	> 10.0	4.4

ED20 - soil-dosis caused 20% inhibition ED50 - soil-dosis caused 50% inhibition

Plant inhibition decreased (growth increased) in contaminated soil treated with RAMEB as consequence of better nutrien availability and of decreased toxicity.

Table 2. *Photobacterium phosphoreum* bioluminescence test

Soil	4 month bioremediation		8 month bioremediation		10 month bioremediation	
	ED20 [mg soil]	ED50 [mg soil]	ED20 [mg soil]	ED50 [mg soil]	ED20 [mg soil]	ED50 [mg soil]
Contaminated	< 3	5	18	> 50	> 50	> 50
Cont. + 0.5 % CD	4	11	30	> 50	> 50	> 50
Cont. + 1.0 %CD	5	10	> 50	> 50	> 50	> 50

ED20 - soil-dosis caused 20% inhibition ED50 - soil-dosis caused 50% inhibition

Encapsulation of the contaminant resulted in decrease in the toxicity.

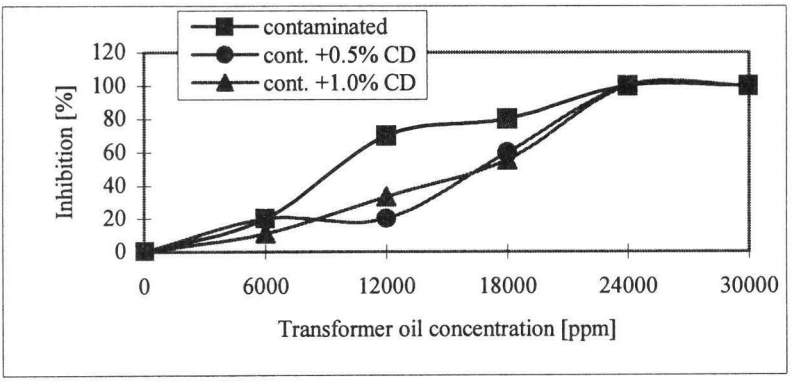


Figure 1. Toxicity for Collembola decreased in the presence of cyclodextrin

References
1. Gruiz, K., Fenyvesi, É., Kriston, É., Molnár, M. and Horváth, B.: Potential use of cyclodextrins in soil bioremediation – J. of Inclusion Phenomena and Mol. Recognition **25,** 233-236, 1996
2. Horváth, B., Gruiz, K. and Sára, B.: Ecotoxicological testing of soil by four bacterial biotests Toxicological and Environmental Chemistry **58**, 223-235, 1996
3. Gruiz, K., Murányi, A., Molnár, M. and Horváth, B.: Risk Assessment of Heavy Metal Contamination in Danube Sediment - J. of Water Sci. and Technol., in press, 1998
4. Riepert,F. and Kula, C.: Development of laboratory methods for testing effects of chemicals and pesticides on Collembola and earthworms, Inst. for Ecotox. **320**, pp. 8-47, 1996

Theme F:
Land reuse, legal and financial development, management of contaminated land

THE VEGETATION OF COVERS FOR LANDFILLS AND CONTAMINATED SITES: MONITORING DATA AND RECOMMENDATIONS

V. Sokollek and A. Seelig-Braker

Ministry of the Environment, Office for Remedial Action, Billstraße 84, D-20539 Hamburg

Key words: Covering system, landfills, monitoring, reuse, vegetation, water balance.

1. Introduction

When contaminated sites or old landfills are isolated by encapsulation, for many reasons a „green" surface, i.e. a vegetation cover on top of the site, is often planned and carried out. The vegetation has to fulfill different purposes, such as

- enhancement of the sealing system functions (e.g. stabilization of the topsoil, high consumption of water, no damage to the liner system),
- making possible the reuse of the area in different ways,
- enhancement of the ecological value of the site.

Under this aspects the question is: which is the most appropriate type of vegetation on multilayered covering systems ?

2. Monitoring of the isolated Georgswerder waste disposal site

The hill-shaped Georgswerder waste disposal site (Hamburg/Germany) of 45 hectars is isolated by a surface sealing system. It consists of a composite liner (HDPE geomembrane above compacted soil liner), overlain by a drainage layer (0.25 to 0.30 m fine gravel) and 0.75 to 2.0 m topsoil (loamy sand and sandy loam). Most of the topsoil has been covered by meadow-type vegetation since 1988. Additionally about 20 % of the area has been planted with bushes and trees in 1995.

A comprehensive monitoring program of the sealing system during the phase of aftercare has been developed. One part of this has been the monitoring of the vegetation since 1989. The monitoring is performed by annual mapping, root growth observations, and heavy metal analyses of plants and soil (due to airborn immissions). Moreover a hydrological monitoring program is carried out to quantify the hydrological impact of the vegetation cover on the system.

So far, the main results of eight years monitoring are as follows:

- Although only about 10 plant species were seeded on the topsoil, over the monitoring period more than 200 species have been found on the covering system. Due to annual mowing, dense meadow vegetation types have developed which ara well adapted to the differing site conditions. The plant cover is stable and able to regenerate, e.g. after drought damage.
- Some ruderal plants with strong, deeply intruding roots (e.g. *Rumex, Armoracia*) are rather frequent. The root intrusion into the drainage layer and possibility of intrusion into the liner system is monitored.
- Several rhizotrones (root growth observation boxes) make evident that the roots of different spezies are able to grow about one meter during one season and can penetrate the drainage layer.
-Water balance studies, based upon intense measurements and calculations during eight years, show that the evapotranspiration of the covering system reaches about 500 mm/year as an average. The U values (precipitation minus runoff; see fig. 1) are a close representation of the amount of water consumption of the vegetation cover. Due to the

dense vegetation, surface runoff is in general very small (about 5 % of yearly total runoff), although slope inclination measures up to 30 %. The drainage layer runoff predominates.

3. Recommendations concerning the vegetation of surface sealing systems

The „ideal" vegetation type for any surface sealing system does not exist. The selction of the vegetation cover depends on site-specific conditions, technical demands, and the planned afteruse and function of the former contaminated site.

In general, four main types of vegetation seem to be possible:

1. Meadow-type vegetation is useful for sites which require intens monitoring in the time of aftercare. Yet, the expenses for treatment (mowing) are comparatively high.
2. Bush vegetation seems to be useful for public parks. This type of vegetation requires little treatment, but the monitoring of the sealing system becomes more difficult.
3. Forest vegetation is useful for sites which are placed in forested areas. Moreover tree stands show the highest evapotranspiration. However, forest requires very thick topsoil of 2 to 3 meters. Problems due to windthrow and deep root intrusion can arise.
4. Natural succession of vegetation without treatment by man seems to be of advantage under cost and ecological aspects. However, it is questionnable whether the vegetation will meat the technical requirements in the long term. Moreover intens monitoring and arbitrary reuse will not be possible.

In many cases combinations of the different vegetation types 1. to 4. on the sealed site are useful, e.g. for recreational and ecological purposes.

References:

- Sokollek, V. and A. Seelig-Braker (1996): Ingenieurbiologische Aspekte bei der Abdeckung von Deponien und Altlasten; K. Czurda and K. Stief (eds.) Oberflächenabdichtung oder Oberflächenabdeckung? *Schriftenr. Angewandte Geologie Karlsruhe 45*, pp. 14/1-21.
- Sokollek, V. and M. Weigelt-McGlone (1997): Der Wasserhaushalt eines großflächigen Oberflächenabdecksystems - Fallbeispiel Deponie Georgswerder (Hamburg); V. Franzius et al. (eds.) Handbuch der Altlastensanierung, 6. Ergänzungslieferung d. 2. Auflage, April 1997, pp. 1-27.

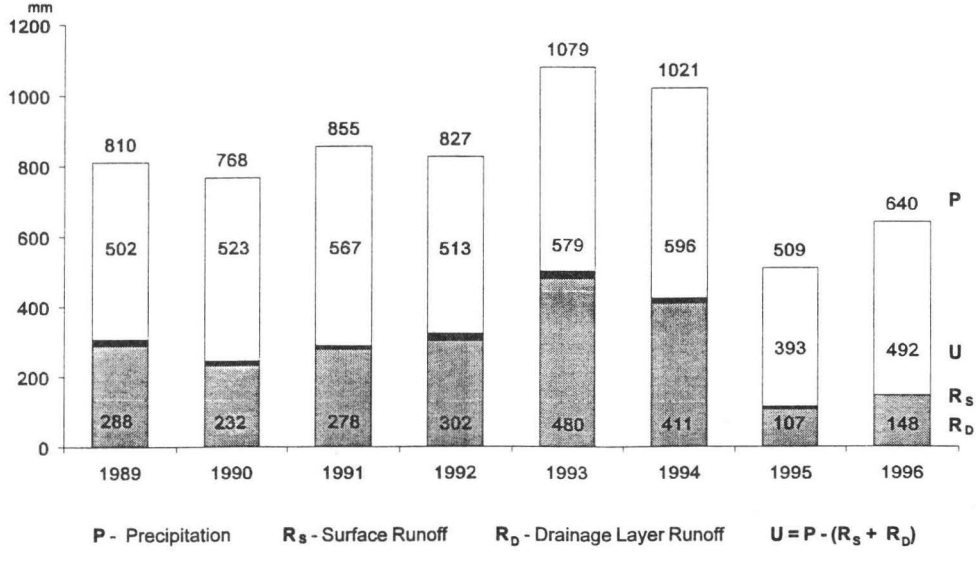


Fig. 1: Yearly water balance 1989-1996 of the hilltop cover (14.3 ha) Hamburg-Georgswerder with meadow-type vegetation. Budgeting periods each from April 1 to March 31.

TRAINING NEEDS FOR CONTAMINATED LAND SPECIALISTS

Paul Nathanail & Judith Nathanail

Centre for Research into the Built Environment, Nottingham Trent University, Nottingham NG1 4BU, UK. crbe@crbe.co.uk

Key words: education and training; knowledge transfer

Contaminated land management is multi-disciplinary, rapidly developing and involves input from, and communication between, a wide range of science, engineering and other professionals. Specialists need to update regularly their skills and knowledge[3,4].

TASK ANALYSIS

Contaminated land management is tackled in four distinct phases. The training required for each phase are summarised below.

Phase 1 Risk Assessment

Training should focus on: collection and collation of existing information on site history and setting, regulatory history; identification of plausible source-pathway-receptor pollutant linkages and design and planning of site investigations.

Phase 2 Risk Assessment

Training will be required in designing, executing and reporting site investigations, geochemical analysis, and risk assessment to provide knowledge of the type of parameters used in risk assessment, how the parameters relate to the predicted ground conditions and how they can be obtained by various methods of investigation and testing. An understanding of sampling errors and uncertainties and the amount of data required is needed. Some experience of site supervision and risk analysis is needed before taking sole charge of planning an investigation.

TABLE 1 CRBE CONTAMINATED LAND MANAGEMENT MSc CONTENTS[5]

Module	Credit points	Status
Balancing studies	5	DL
Professional practice	5	C
Environmental legislation	5	C
Environmental geology	5	C
Environmental Geochemistry	3	C
Meteorology	2	C
Site characterisation	5	C
Risk Assessment	10	C
Remediation	10	C
Waste management	5	C
Toxicology	2	C
Epidemiology	3	C
Field trip	5	C
Conventional remediation	5	O
Innovative remedial technologies	5	O
Implementing remedation	5	O
Risk modelling	5	O
Geostatistics	5	O
GIS	5	O
Dissertation	40	C

DL: Distance learning; C: Core; O: Optional

Phase 3 Remediation

Training is required to ensure an understanding of the strengths, limitations and operational requirements of each of over 25 remediation strategies[2] and in how to objectively select the optimum strategy given site specific constraints.

Phase 4 Monitoring and validation

Monitoring and validating remediation are forms of site investigation and risk assessment and training requirements are similar to Phase 2. Additional training

may be required to meet specific requirements of legal, valuation and insurance professionals.

TRAINING REQUIREMENTS ANALYSIS

The tasks contaminated land managers have include: liaison with science, engineering and non technical professionals; environmental geochemistry; contaminant hydrogeology; site investigation of potentially hazardous ground; risk assessment; selection of remedial strategy; implementation of remediation; use of computers for data analysis, ground characterisation and risk assessment (Table 1).

They also require knowledge of the following areas: environmental legislation and policy; toxicology & epidemiology; waste management; valuation, environmental economics and insurance.

OPTIONS ANALYSIS

Training needs can be met through: undergraduate education ; post graduate education and training; on the job training and continuous professional development (CPD).

Undergraduate education is the first of many stepping stones. Education at this level could be directed towards providing knowledge about contaminated land with a view to creating an intellectual framework which enables that knowledge to be used and further knowledge to be gained[1].

Post graduate courses have been developed at several British Universities. Masters courses should provide specialist knowledge and skills and develop a logical problem solving approach, using real examples where possible[5] (Table 1).

Much essential knowledge can be acquired 'on the job'. Methodology, terminology, project management, technology performance, client needs and constraints can all be best studied in the 'real world'. However experience should cover a broad range of subjects. Professional experience should be structured to provide both variety and depth in the skills the contaminated land specialist will need throughout her career[3].

Most professional societies include low cost CPD events in their programmes. Details of some are at **http://www.fesweb.ntu.ac.uk/cbe/focil/focil001.htm**.

REFERENCES

1. DE FREITAS, M. H. 1994. Teaching and training in Engineering Geology: Professional practice and registration. *In:* OLIVEIRA R.ET AL. (EDS), *Proc 7th Int Cong IAEG,* Vol **V1**, LVII - LXXV, A. A. Balkema, Rotterdam.

2. MARTIN I. & BARDOS P. 1995. *A review of full scale treatment technologies for the remediation of contaminated soil*, EPP Publications, Richmond.

3. NATHANAIL, C. P. & NATHANAIL, J. 1996. A (draft) training guide for geologists in the contaminated land assessment and remediation industry. *In:* LERNER, D. & WALTON, N. (EDS) *Pre prints Engineering Group Conference: Contaminated Land and Groundwater - Future Directions*, Portsmouth University, 359-378.

4. NATHANAIL, C. P. & NATHANAIL, J. 1998. Professional training for geologists in contaminated land management. *In:* LERNER, D. & WALTON, N. (EDS) *Engineering Geology Special Publication: Contaminated Land and Groundwater - Future Directions*, Geological Society Publishing House (in press).

5. NATHANAIL, C. P. 1997. *MSc Contaminated Land Management.* CRBE, Nottingham.

FINANCING REMEDIATION OF CONTAMINATED SITES IN AUSTRIA

Thomas Steirer

Österreichische Kommunalkredit AG, Türkenstr.9, A-1090 Wien, Austria

Key words: contaminated sites, support, guidelines, industrial sites, land register, landfill site, priority list, program, site investigation

SUMMARY

Since 1989 the implementation and financing of contaminated sites remediation in Austria is based on a legal act, the Federal Remediation Act. Since then the amount of ECU 136 mio. has been levied as a Contaminated Sites Charge. This money is used for investigation and site remediation in all provinces of Austria.

133 sites are registered in the Contaminated Sites Inventory. The financing of site remediation is based on a Support Program and the Support Guidelines of the Federal Minister of Environment. Österreichische Kommunalkredit AG administers the Support Programm on behalf of the Federal Minister of Environment. Up to now about ECU 245 mio. have been allocated, ECU 72 mio. have been paid out.

KURZFASSUNG

Seit 1989 gibt es für die Durchführung und Finanzierung der Altlastensanierung in Österreich eine rechtliche Grundlage, das Altlastensanierungsgesetz. Seit damals wurden rund ECU 136 Mio. an Altlastenbeiträgen eingehoben. Diese werden bundesweit für Untersuchungen bei Verdachtsflächen sowie für Sanierungsmaßnahmen bei Altlasten verwendet.

133 sanierungsbedürftige Altlasten sind im sogenannten Altlastenatlas verzeichnet. Auf Grundlage des Förderungsprogrammes und der Förderungsrichtlinien des Bundesministers für Umwelt werden die Fördermittel zugeteilt. Die Abwicklung der Förderung im Auftrag des Bundesminister für Umwelt hat die Österreichische Kommunalkredit übernommen. Bisher sind rund ECU 245 Mio für Sanierungsmaßnahmen genehmigt worden. Davon sind ECU 72 Mio. bereits ausbezahlt.

Contaminated Soil '98, Thomas Telford, London, 1998, 1215–1217

FEDERAL REMEDIATION ACT

The Federal Remediation Act was established in 1989. It regulates the investigation and assessment of contaminated sites, the legal procedures and the financing of remediation. Based on the act a „Contaminated Sites Charge" can be levied from the landfill operators. The charge level depends on the weight and type of waste and technical equipment of the landfill. The level will increase every two years in order to stimulate waste avoidance and thermal waste treatment.

REGISTER OF POTENTIAL CONTAMINATED SITES

The Provincial Governments are committed to report potential contamiated sites to the Federal Ministry of Environment. Till the end of 1997 a number of 2584 sites have been included in the Register of Potential Contaminated Sites. About 93 % of them are landfills, most of them municipal and already inactive, 7 % are industrial sites. After a rough estimation of risks, the Federal Ministry of Environment decides, if additional investigations are necessary to complete the risk assessments. These investigations can be financed out of the revenue of the Contaminated Sites Charge.

CONTAMINATED SITES INVENTORY

After the risk assessment and the classification of priority the sites are included in the Contaminated Sites Inventory edited by the Federal Ministry of Environment. The Inventory currently comprises 133 sites and their environmental risks. 32 sites are of highest priority (Class 1). The relation between landfills (54 %) and industrial sites (46 %) in the Inventory differs very much from the Register of Potential Contaminated Sites. This may be explained by the fact, that the investigations of especially the municipial waste sites are for the most part done, while the investigation programs of possible contaminated industrial sites are still running, and only the well known industrial sites are already registered in the Inventory.

CONTAMINATED SITES CHARGE

In 1998 the rates of the Contaminated Sites Charge for depositing are:

excavated soil	ECU 5,80
demolition waste	ECU 5,80
municipal waste	ECU 14,40.

An additional charge is levied for missing leachate catchments in the landfill (+ ECU 28,80) and missing landfill gas collecting (+ ECU 28,80).
From 1990 till 1997, over ECU 139 mio have been levied by the financial authorities.
15 % of the revenue may be spent for additional site investigations; 85 % are reserved for the remediation support.

SUPPORT PROGRAMM

The Support Programm for Contaminated Sites covers those sites registered in the Inventory where no remediation measures have been started or the funding of the measures is not guaranteed. As a preparation for the support decisions, the sites are ranked according to the following criteria:

priority class	financing situation
quality and maturity of project	legal authorization

SUPPORT GUIDELINES

In 1997 new Support Guidelines were issued by the Federal Minister of Environment. The different support rates depend on the status of the recipient (private : 15%-40%, public : up to 65%). These rates are in conformity with the European Support Regulations and shall not influence the economic competition. Special exceptions are provided for the remediation of abandoned sites or damages originating from WW II (rates up to 95 %).

IMPLEMENTATION 1990-1997

In 1990 the first site investigations financed out of the Contaminated Site Charge were carried out. Since then investigation programs on 31 sites were finished; 147 are still running. Therefore ECU 5,1 mio. have already been paid out; ECU 13,8 mio. are reserved for the running programs.

The first support contracts for site remediations were concluded in 1991. Since then a total support-amount of ECU 245 mio. was allocated by the Federal Minister of Environment.

Österreichische Kommunalkredit AG administers the Support Program on behalf of the Federal Minister of Environment, including project evaluation, decision preparing, contracting and controlling.

Over ECU 72 mio. have already been paid out for the remediation of 68 contaminated sites. 30 sites are completely cleaned-up or at least made safe with temporary measures.

PROSPECT

Running site investigation programs will result the remediation of a lot of sites in the future. Increasing revenues from the Contaminated Sites Charges will guarantee the possibility of supporting further remediations. Due to higher support rates for municipial and abandoned sites in the new guidelines, the support applications will probably focus on this areas.
A re-enactment of the Federal Remediation Act shall bring about better legal instruments to force responsible polluters and site owners to remediation.
R&D-projects for the improvement and the development of Clean-Up technologies will be stimulated by new support possibilities.

ASSESSING THE DURABILITY OF BUILDING MATERIALS IN CONTAMINATED LAND

Stephen L Garvin, Julian P Ridal and Max Halliwell
Building Research Establishment, Scottish Laboratory, East Kilbride, G75 0RZ, Scotland, UK

Key Words : contaminated land, buildings, degradation, remediation, sulfates.

Summary
Building materials may be subject to degradation from contaminants introduced to the ground from industrial activities. It is well known that sulfates and acids affect concrete but uncertain as to how other contaminants may cause deterioration or enhance attack. This paper describes experimental and field studies intended to address these uncertainties.

Introduction

Building on a contaminated site may take place either as an integral part of the remediation or after the site has been decontaminated. There are several options for remediation and it is not uncommon to leave the contamination in place and build on the ground taking suitable precautions for protection of the building and its occupiers. This does leave a risk that contaminants in the ground will attack the materials used to construct buildings. For this reason experimental studies have been undertaken since 1993 to assess the effect of contaminants on building materials.

Experimental

Laboratory studies have included immersion of concrete cubes in solutions of contaminants. The solutions were formulated on the basis of concentrations of contaminants which were reported in site investigation reports of former gasworks, steelworks and scrap yard sites. Data on metals and salts were used together with aggressive concentrations of sulfate (4,200 mg/l - class 4 sulfate) and low pH conditions. In total six solutions have been used; four (solutions A - D) have a mixture of contaminants and two are used for comparison which contain only sulfate (solution E and F). A water control solution was also used for comparative purposes.

Concrete cubes (100 mm) were made from nine different concrete mixes. The cement type and content was varied to give a range of materials that were either considered resistant or susceptible to the contamination, in accordance with BRE Digest 363. Three Portland cement (OPC) concretes, two blastfurnace slag (ggbs), two fly ash (pfa), a sulfate resisting cement (SRPC) and a BRECEM (HAC:ggbs) were all used. Samples of the concrete cubes were removed from the solutions after one and three years for test, in addition three concrete mixes were deteriorating so badly that samples were removed for test after two years. These three mixes were all recognised as not being resistant to the effects of high levels of sulfate.

Results

The OPC concrete were all found to have lost strength over the period, in particular mixes 2 and 3 which had the higher cement contents. In this respect mix 1 has performed much better

than would have been expected. Part of the reason for the better performance was that it was necessary to add a superplasticiser in order to obtain the required workability from the mix, in turn this reduced the water demand and produced a dense concrete.

The blastfurnace slag mixes (4 and 5) were found to perform differently. Mix 4 with the lower cement content and higher w/c ratio increased strength over the first year, in some solutions to the same extent as the control solution (water). Between one and two years considerable loss of strength was observed in all solutions, and this was coupled with visible deterioration of the cubes. In some cases the loss of strength between two and three years was not significant, but further strength loss was noted in the acidified solutions. The better ggbs mix had gained strength over the first year in all solutions. From one to three years strength loss has been found for all the solutions, especially those acidified solutions.

The two OPC/pfa concrete mixes (6 and 7) have both performed well over the three years. After one year both mixes had gained strength in all solutions and there was little sign of chemical attack. The acidified solutions caused a retardation of the strength gain and after three years the cubes had lost some strength in comparison with the 28 day value.

The SRPC concrete generally gained some strength over the first year. Between one and three years loss of strength was noted in all the solutions apart from the water control (G). However, the SRPC concrete had a high 28 day strength (73.5 N/mm^2) and unlike concrete with ggbs and pfa would not be expected to significantly gain strength after this time. The BRECEM mix had a low 28 day strength (21.0 N/mm2) but was found to gain strength significantly by both 1 and 3 years, apart from some loss in the acidified solutions after one year.

The conclusions of the research after three years were as follows:

- the acidified solutions were causing greater deterioration and loss of strength than neutral solutions
- the mixed solutions of contaminants enhanced deterioration and strength loss in comparison with single sulfate solution.

Field Trial

The solution tests are accelerated tests and give an indication of the total potential effect of contaminants on the building material. Therefore, it was decided that field studies should be initiated to assess the performance of concrete and other materials under contaminated soil conditions. Funding has been provided by the UK's Department of the Environment, Transport and the Regions and industry partners in order to carry out this research. After contacting numerous owners of contaminated land sites, a former steelmaking plant in North Wales was made available by the landowner. The ground contains sulfates, metals, organics and other contaminants. The field trial has included concrete in the form of precast piles and cast in-situ piles. A number of mixes were used, all of which were considered to be resistant to the effects of contaminants. They included OPC, OPC/ggbs, OPC/pfa, OPC/microsilica and SRPC concrete. Samples of steel piling and concrete blockwork masonry were also installed in the contaminated site. Samples will be retrieved from the site after 1, 5 and 10 years and assessment made of any deterioration that has occurred.

EXHAUSTIVE CONTROL OF A CONSTRUCTION PROJECT IN CONTAMINATED SOIL

F. Travesa[1], V. Colomer[1], J. Rius[1] and B. Mundó[1]

[1] TQMA, S.L., Carrer 4, s/n, sector C, Edificio CESPA, GR. 08040 Barcelona. Spain

Key words: contaminated soil, risk analysis, VOCs, chlorinated hydrocarbons, plant, excavation, inventory, management.

The need for land within Industrial Polygones, in the surroundings areas of big cities like Barcelona, is very important.

The Industrial Polygone of Prat, in the Delta of the river Llobregat, near Barcelona, is considered to be one of the most suitable given it's location and services. In this case, an Industrial group based in the above mentioned polygone decided on expanding it's business. To do so it needed the nearby plots which were before occupied by a solvent recuperation plant who after on a joint-venture with a company of similar characteristics move to another Polygone Industrial. The solvent recuperation plant was for distilation obtaining solvent product and two wastes. Our study started while the solvent recuperation plant was still running.

The work consited of a soil pre-evaluation which allowed decided an adequate use of the terrain according to future activities. Once having seen the viability of the study, an exhaustive control of the construction project took place in order to comply with the legalities imposed by the Junta de Residus de la Generalitat de Catalunya (local EPA).These rules are still in a project phase and will constitute the quality specifications of polluted soil for the future land-law of Catalunya.

The work here described is one of the first to be done according to the emerging quality specifications in Catalunya.

In order to carry out the project certain acts were carried out in different phases:

1. PRE STUDY OF SOIL CONTAMINATION : ESTABLISH NEW USE OF SOIL
2. SOLVENT PLANT DISMANTLING CONTROL : A PREVENTIVE ACTION TO AVOID INCREASE OF CONTAMINATION.
3. CONTROL SOIL REMOVE : TO ENSURE A CORRECT MANAGEMENT OF CONTAMINATED SOIL.
4. HIDROGEOLOGICAL STUDY AND RISK ANALYSIS : TO CHECK A ACCOMPLISHMENT OF QUALITY ESPECIFICATION AND ASSOCIATED RISK.

Table 1: The four fhases of this project.

1. Pre study of soil contamination

a) Historical review

b) Site characteristics :

- Area of the plant: 15.000 m^2.
- 1,5 metres of filling materials deposited on autochthonons silt.
- Waste pond of 3.000 m^3.
- Basic contamination through SVOC's, VOC's and Chlorinated Hydrocarbons.

c) Exploratory boring

2. Dismantling control

a) Plant inventory

b) Inspection of all the dismantling works of the plant:

- Previous inspection of the installations (tanks and boilers, refrigeration towers, laboratories, store rooms, offices) and Management of left-over waste of the plant.
- Cleaning: tanks, pipes, equipment and installations.
- Supervision of all demolishments, breaking up and dismantling.

3. Control of soil remove

a) Rehabilitation of waste pond

- Characterization, excavation, removal and management of wastes.
- Standarized work methods according to international security standards (EPA SW-846, ASTM 4687).

b) Excavation and management of the plant site.

- Division of the plant in 128 allotments of 150 m^3 (35m x 6m x 0,7m)
- Excavation and different store of each allotment
- Sampling and quarter
- Sample analysis, qualification and deciding on the destiny of the soil :
  - Contaminated soil (waste) 15.013 ton
  - Contaminated industrial soil 14.586 ton
  - No contaminated soil 9.262 ton

4. Hidrogeological study and risk analysis

a) Exploratory boring: 39 exploratory boring in the areas that have been excavated, column description and sample analysis.

b) Hidrogeological study: the hidrogeological characteristics of the area and the analitical results show a difficulty in moving the existing contaminating agents in the soil of the plant.

c) Risk analysis: Analysis of soil samples

- Use of the programmes SOLUTE and HUMAN RISK to measure the risk dispersion of aquifer contamination, and the health of the population.

RESULTS

- EXHAUSTIVE CONTROL OF THE DETECTED CONTAMINATION.
- OPTIMIZATION OF THE COSTS CONCERNING THE SOIL MANAGEMENT.
- USE OF THE LAND WITH A NEW ACTIVITY WITHOUT CAUSING A RISK FOR PUBLIC HEALTH OR ENVIROMENT.

Table 2: Results of the project.

MONITORING THE RECLAMATION OF ACIDIC SPOIL FOR AMENITY WOODLAND

K.V. Heal[1], C.A. Salt[1], I.C. Grieve[1] and J.A. Hipkin[2]
[1] Department of Environmental Science, University of Stirling, Stirling FK9 4LA, UK
[2] Andrew Hipkin Associates, 9 Livilands Gate, Stirling FK8 2AT, UK

Key words: acid-mine drainage, mine waste, remediation, leachates, monitoring

RECLAMATION PROGRAMME

The Benhar ironstone spoil heap covers 5 ha and is located at 230 m elevation in the headwaters of the River Almond, Central Scotland, UK. Until recently the spoil heap was unvegetated and generated highly acidic, metal-rich drainage[1]. Since March '97 the site is being reclaimed by Central Scotland Countryside Trust in collaboration with the University of Stirling. The following treatments were incorporated into the spoil at about 0.5 m depth: dried pelleted sewage sludge (BIOGRAN) at 35 t ha^{-1}, peat at 30 t ha^{-1}, coarse limestone chips at 60 t ha^{-1}, and ground limestone at 30 t ha^{-1}. After conventional forestry ploughing common alder (*Alnus glutinosa*) and downy birch (*Betula pubescens*) were planted in May '97. A settling pond and surface water wetland of 0.4 ha were constructed below the spoil heap to treat drainage. The wetland substrate of mushroom compost on crushed limestone was planted with cattail (*Typha latifolia*) in August '97. A 3 year monitoring programme began in June to record changes in drainage water chemistry and wetland performance. Monthly water samples are collected from 18 *in-situ* samplers, installed at about 0.3 m depth, and from sites upstream and downstream of the wetland. pH, alkalinity/acidity, nitrate, molybdate reactive phosphate, sulphate, total Fe, Al and Mn, and dissolved Fe, Mn, Al, Ca, Mg and K are measured in the samples.

WETLAND TREATMENT RESULTS

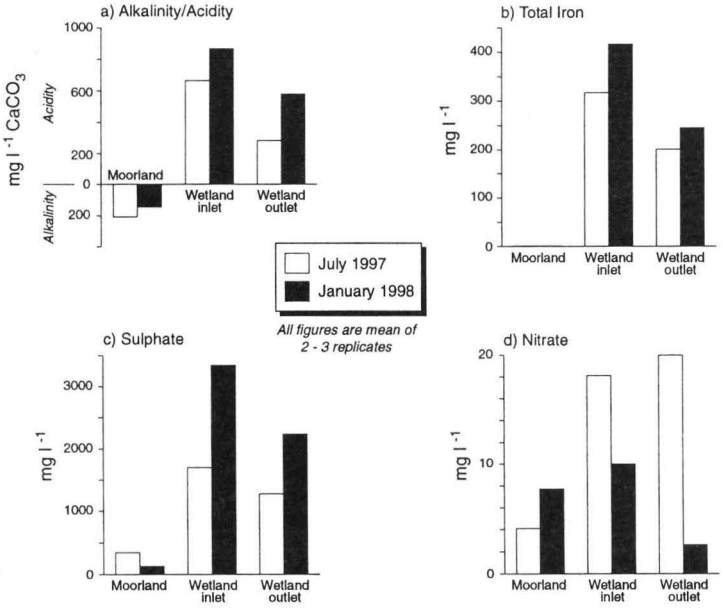


Figure 1. Comparison of site drainage parameters, July 1997 and January 1998

Contaminated Soil '98, Thomas Telford, London, 1998, 1223–1224

Fig. 1 compares selected parameters in moorland drainage upstream of the spoil heap, and at the wetland inlet and outlet in July '97 and Jan '98. Acid-mine drainage inputs are apparent from the increases in acidity, total Fe and sulphate between the moorland and wetland inlet. Wetland treatment is improving water quality, as shown by reduced total Fe, acidity and sulphate concentrations at the wetland outlet compared to the inlet. Wetter antecedent conditions are likely to have caused the increase in acidity, total Fe and sulphate from Jul 97 to Jan 98 at the inlet (antecedent rainfall = 105.5 mm Jul 97, = 127.0 mm Jan 98). The resultant loading on the wetland system has lead to water quality deterioration at the outlet, although the system is still effective in removing acidity, total Fe and sulphate. The rise in nitrate concentration between the moorland and wetland inlet in Jul 97 (Fig. 1d) suggests that amendment of the spoil material with BIOGRAN may have increased nitrate leaching. However, this effect appears temporary as less nitrate was measured in Jan 98.

SPOIL THROUGHFLOW RESULTS

Table 1 shows the same parameters measured in throughflow from the spoil in Jul 97 and Jan 98. Spoil amendment has lowered acidity, total Fe and sulphate concentrations in near-surface throughflow compared to the wetland inlet site which receives deeper drainage from the spoil heap (compare Fig. 1 & Tab. 1). However, the range of values in Tab 1 indicates that acidity-generating "hotspots" remain in the spoil. Exceptionally high nitrate concentrations in throughflow in July are attributed to rapid nitrate leaching after spoil amendment with BIOGRAN since values are much lower in Jan 98.

	July 1997	*January 1998*
Acidity	N/A	73 (22-836)
Total Fe	0.2 (0-1.0)	0.5 (0.1-439)
Sulphate	1505 (590-2017)	2159 (1137-6017)
Nitrate	604 (81-1547)	76 (1.3-643)

Table 1. Throughflow chemistry for all *in-situ* samplers, July 1997 and January 1998
(All units mg l^{-1}. Median values shown with range in brackets).

CONCLUSIONS

Spoil amendment has improved the quality of throughflow from the Benhar spoil heap but there has been no discernible improvement in nearby surface watercourses. The wetland treatment system has effectively lowered acidity, sulphate and total Fe concentrations in surface drainage. Comparison of initial Fe retention calculations[2] with values for similar wetland treatment systems in the USA[3] suggest that the wetland is under performing. Future monitoring will determine whether: (i) performance improves as cattail becomes established, (ii) performance varies seasonally, and (iii) spoil amendment improves the quality of deep drainage from the spoil.

ACKNOWLEDGEMENTS
We thank Titus Barthram (Hartwood Research Station, MLURI) for making available the rainfall data.

[1] Burrows, M. (1996). *Site assessment for an artificial wetland to ameliorate acid mine drainage*. BSc thesis, University of Stirling.
[2] Cudden, J.R. (1997). *The effects of the reclamation of acid mine spoil on water draining Benhar ironstone Bing*, Central Scotland. MSc thesis, University of Stirling.
[3] Wieder, R.K. (1993). Ion input-output budgets for five wetlands constructed for coal mine drainage treatment. *Water, Air and Soil Pollution 71*, 231-270.

Utilising Contaminated and Disturbed Industrial Land for Short Rotation Coppice

S Rees, ID Pulford & HJ Duncan
Environmental Chemistry, University of Glasgow, Glasgow. G12 8QQ.

Keywords: Contaminated soil, in-situ bioremediation, clean-up technologies.

Background

Interest in the growth of Short Rotation Coppice (SRC) as an alternative to arable crops has generated a significant amount of research in recent years. Currently in the UK returns from SRC on prime arable land under open market conditions are insufficient for its large scale adoption. As an alternative to agricultural land the potential for utilising disturbed industrial land presents significant opportunities. In Scotland alone approximately 12,000ha of such land has been identified (Scottish Office,1990), with England and Wales having an additional 40,000ha. (HMSO, 1988) The nature of many of these sites does not lend itself to a high production potential for SRC. Consideration of additional opportunities which might prevail, such as environmental gains through site enhancement, sewage sludge disposal, decontamination by metal uptake and the provision of a carbon sink, along with the possibility of an economic return from the sale of SRC for biofuel or as a fibre crop, does put a new perspective to the equation.

The Field Trial

To assess the potential for SRC production on contaminated and disturbed industrial land a field trial was established on the site of the former Hallside steelworks site, approximately 7 miles from Glasgow. With the closure of the steelworks in 1979, the 32 ha had remained derelict and vacant until recently when a project achieved in collaboration between The Scottish Greenbelt Company and developers saw the capping of the site with colliery spoil amended with sewage sludge.

Two trials have been established to consider:

1) the effects of silvicultural practices (weed control, fertiliser application, row spacing and cutting frequency on the yields of 5 willow clones chosen for their performance on a sacrificed agricultural site used for the disposal of sewage sludge for over 40 years.(Riddell-Black et al,1997): A Rosewarne White (*S. aurea x cinerea x viminalis)*,B Bujatica Germany (*S. burjatica),* C Dasyclados (*S. caprea x cinerea x viminalis*, D Gigantea (*S.viminalis*), E Spaethii (*S.spaethii).*
2) The suitability of 20 willow clones for growing in this medium.

Results

Initial results for the survival rates of individual clones against treatments have shown wide variations, the same is also observed for the 20 clones. A limited selection of treatments against clones is reproduced in table 1 and a complete breakdown of the survival of the 20 clones is reproduced in table 2.

Table 1. Variations in survival rates against treatments.

Treatment	Clone A % Surviving	Clone B % Surviving	Clone C % Surviving	Clone D % Surviving	Clone E % Surviving
Whole Site	42.02	49.82	61.47	54.21	28.66
0.5M Spacing	33.7	44.6	59.15	53.74	27.18
0.5M Spacing - NWC	21.29	28.32	40.74	44.96	18.76
0.5M Spacing - CWC	54.1	60.88	77.56	62.51	35.6
1.0M Spacing	44.8	55.04	62.86	52.78	30.13
1.0M Spacing - NWC	36.62	42.93	53.44	43.85	18.57
1.0M Spacing - CWC	52.97	67.14	72.28	61.7	41.69

Key - NWC - No Weed Control CWC - Chemical Weed Control

Table 2. Survival Rates for 22 willow clones

Clone		Area 1	Area 2	Average
1	Q83	6.7	20	13.3
2	Calodendron	10	3.3	6.7
3	Jorrunn	66.7	53.3	60
4	Campbell 3106	56.7	66.7	61.7
5	Spaethi	26.7	23.3	25
6	Ninians Prunifolia	3.3	0	1.7
7	Candida	76.7	33.3	55
8	Delamere	70	33.3	51.7
9	Torra	60	30	45
10	Gigantea	70	10	40
11	Stipularis	0	20	10
12	Biorn	30	*	30
13	Orm	36.7	13.3	25
14	Rapp	6.7	23.3	15
15	Dasyclados	0	40	20
16	Jorr	63.3	*	63.3
17	Coles	46.7	0	23.3
18	Ulv	30	30	30
19	Rosewarne White	*	20	20
20	77699	*	50	50

Area 1 - Compacted Substrate Limited Weed Establishment
Area 2 - Structured Substrate Severe weed competition

Conclusions

Early indications of the potential for utilising disturbed and contaminated land for the establishment of SRC have shown large variations in the survival rates of individual clones. The importance of effective weed control is apparent, particularly on this rehabilitated site where weed invasion has been severe. Implementing an effective weed control programme may provide a short term solution, however given the narrow economic constraints upon such sites this measure may not provide a cost effective solution in the long run. A more effective approach may be to select those clones which are able to out-compete weed growth and hence limit the need for weed control altogether. Differences in the growth patterns and survival rates of the various willow clones are very apparent, collating this information and putting it to a constructive use could provide a solution to the growth of SRC on such sites.

Acknowledgement

We are grateful for funding for this work from the Scottish Greenbelt Foundation.

FINANCING THE REMEDIATION OF CONTAMINATED SITES

M. Lowe[1], O. van Sandick[2] and R. Salter[3]

[1] Department of the Environment, Transport and the Regions, Ashdown House, 123 Victoria Street, London SW1E 6DE, UK
[2] Ministry VROM/DGM, Directie Bodem, Code 625, 2500 GX The Hague, The Netherlands
[3] Ministry for the Environment, Pollution and Risk Management Directorate, 84 Boulcott Street, PO Box 10362, Wellington, New Zealand

Key words: contaminated sites, environmental policy instruments, government, industrial areas, land register, legislation, liability, planning, redevelopment, regeneration.

INTRODUCTION

Funding is an essential part of any approach to the remediation of contaminated sites, whether this is being considered at the level of an individual site or as part of a overall national programme. The experience of policy-makers internationally, who have attempted to devise their own national funding frameworks, is that there is no simple solution. Furthermore, the apparent lessons learnt in one country do not necessarily transfer readily to the circumstances of other countries.

This paper summarises detailed discussions in the Common Forum of EU Member States (meeting at Stockholm in September 1996) and the Ad Hoc International Working Group (meeting at Amsterdam in May 1997) on the question of financing the remediation of contaminated sites.

FACTORS INFLUENCING THE FUNDING OF REMEDIATION

It is unlikely that a single funding scheme will meet the needs and circumstances of all the contaminated sites requiring remediation within any country or region. This implies that policy-makers will need to develop a portfolio of different funding approaches. Indeed, this is likely to occur without any conscious effort or intervention by policy-makers, as much site remediation takes place as part of the normal commercial redevelopment of land and not as part of specific environmental improvement programmes.

The success of any individual funding scheme will be affected by, and will itself affect, wider aspects of contaminated land policy (such as questions of "standards"), as well as other funding schemes. (For example, the existence of a strong legal liability framework may encourage problem-holders to remediate sites on a voluntary basis, but may also scare away private investment in the redevelopment of sites.)

The potential success of any suggested funding scheme - or, indeed, of the overall framework for funding - will depend on the answers to the following questions:

- will it be possible to get the scheme implemented? Is it acceptable to the key political, economic and administrative decision-makers?
- will the scheme actually be capable of yielding enough money to achieve its objectives?

The answers to these questions will be dependent on a wide range of factors specific to the particular country or region. These are likely to include:

- *site characteristics.* eg. the particular profile, in terms of nature and origin, of a "typical" contaminated site in the area;
- *socio-political factors.* eg. the political "will" behind remediation, public perceptions, and the political acceptability of taxation and state intervention;
- *economic factors.* eg. the level of prosperity of the area, the nature and strength of local property markets, and the "economic history" of contaminating industries;
- *legal factors.*
- *complementary policy initiatives.* eg. economic regeneration programmes in former industrial areas, and systems of land-use planning and control.

TYPES OF FUNDING APPROACH

It is likely that these factors will not only vary considerably between different countries and regions, but will also impact differently on different types of funding scheme. Some examples of relevant factors, and how they affect four broad types of funding scheme, are set out below:

- *liability regimes* - legally-enforceable requirements on companies or individuals to carry out or fund the remediation of particular sites. The nature and applicability of these regimes will be affected by questions such as whether the original polluting industries still exist, what political will exists to impose a "polluter pays" approach to past activities, and whether this is legally possible.
- *voluntary programmes* - company or industry-sector programmes for the remediation of sites for which they are "responsible". These will be dependent on the micro-economic structure of the particular industry sector, the strength and mobilisation of public opinion, and the strength of equivalent liability regimes.
- *public subsidy* - direct funding for remediation from general or hypothecated taxation. The acceptability of this approach will depend on general political attitudes to levels of taxation; this approach can also serve to undermine liability-driven approaches. Particular forms of taxes will also need to reflect the transaction costs of collecting and distributing the taxes.
- *economic regeneration/site redevelopment programmes* - remediation carried out as part of the redevelopment or reclamation of the land for primarily social, economic or commercial reasons. The success of these in achieving environmental objectives will depend on market prices for land, restrictions on greenfield developments, the overall strength of the economy and the location of contaminated sites in comparison with areas of potential economic growth.

CONCLUSIONS

A more detailed, and developed, understanding of the numerous factors affecting the financing of the remediation of contaminated sites is an important goal for policy-makers. This will help positively in the development and refinement of national approaches to this issue - assisting policy-makers in designing new funding schemes. It will also help policy-makers to resist the inappropriate importing of schemes from other countries, where the circumstances affecting their potential success may be very different.

THE RELOCATION OF A FOOTBALL STADIUM ONTO A CLOSED LANDFILL

P A Braithwaite and P D Wright

Ove Arup and Partners
Edgbaston House, 3 Duchess Place Edgbaston, Birmingham B16 8NH England

KEYWORDS: Aquifer, Environmental risks, Excavation, Landfill gas, Landfill leachate, Modelling of ground water flow, Piling, Redevelopment, Reuse (of sites), Soil and groundwater contamination.

Faced with increasing legislative pressure to provide greater safety at sports stadia, combined with growing resistance to Greenfield Development, Reading Football Club took the decision to redevelop their stadium on a brown field site. Working closely with Reading Borough Council two possible sites were identified. Both sites were contaminated and following financial and technical studies of each site, Smallmead Tip was chosen as the preferred location.

Smallmead tip was a 25ha closed landraise, comprising mainly domestic and commercial waste, that had been in operation between 1974 and 1986. The tip was developed during the times of little regulation under the philosophy of 'dilute and disperse'. The site is underlain by an impersistent layer of alluvial clay, below which lay Terrace Gravels, a varying thickness of London Clay, Reading Beds and Upper Chalk. The waste had been deposited to a depth of up to 7m directly on top of the alluvial clay, which had in places been removed to expose the Terrace Gravels and thus allow leachate to flow from the waste into the underlying strata. The waste had been capped using clay of varying quality and thickness. The cap varied in thickness between 0.2 and 1.8 m with no specific measures to vent or manage the production of landfill gas.

The reclamation strategy was developed to allow construction of the stadium on the landraise. This involved retrofitting leachate and gas controls and monitoring systems and constructing an engineered cap over the fill. A three dimensional hydrogeological model was developed to simulate the complex groundwater flows that existed beneath the site to aid the development of these control systems. Well pumping trials were undertaken to validate the model and allow the design of the abstraction system that was to be used to control the groundwater.

In order to offset some of the reclamation costs, waste from a 6.5ha area of the site was removed to create an area, saleable at normal market value, suitable for retail development. Only Special Waste that was uncovered during the earthworks was taken off site, the remainder was redeposited on the undisturbed waste on which the stadium and car parks would be constructed. This work was carried out under a Waste Management Licence.

The philosophy for the strategy was to ensure that, as a minimum, the conditions with regard to levels of contamination both on and below the site were not made any worse as a result of the development, with the likelihood that they might improve in the longer term.

The leachate control system was designed to perform two distinct functions: to control leachate levels within the existing waste and to control groundwater flow immediately below the waste should elevated levels of contamination be detected in the Terrace Gravels groundwater.

Within the waste the leachate system comprised vertical, 40mm thick, geocomposite drains installed to depths of 7m. These drains also formed part of the landfill gas venting system. Leachate levels were maintained below 1m above the base of the waste by dipping at key locations and pumping out where necessary.

The groundwater abstraction system consisted of well points at 3m centres, in sections along the full length of the boundary. If contamination within the Terrace Gravels groundwater reached an agreed 'trigger level', the abstraction system would be switched on, and remain on until the readings returned to an agreed background level.

In order to reuse the maximum amount of existing capping material a composite with an integral gas-venting layer was designed. The cap comprised a welded LDPE liner, sandwiched between a 6mm geocomposite on the bottom, which provided the gas blanket and offered high puncture resistance and a 750g/m protection felt on top. This was overlain by 750mm of clay recovered from the existing cap that provided physical separation from the infrastructure construction that was to follow.

Piling to support the stadium penetrated through the waste, Terrace Gravels, London Clay and into the top of the Reading Beds. This could have introduced a preferential drainage path down into the Chalk Aquifer. A risk assessment was made to compare various pile types and methods of installation considering the risk associated with fewer penetrations of large diameter cast-in-situ piles against multiple penetrations using small diameter piles such as Continuous Flight Auger (CFA). CFA piles were adopted as being the most suitable for this application.

The reclamation works are now virtually complete; funding has been secured for the retail park which is now being developed; piling has been completed and the stadium construction is underway. During construction the monitoring and control systems have proved successful and the objective of the strategy have been met.

Country sessions

Country Session Germany

Dr. Fritz Holzwarth, Federal Ministry for the Environment, Nature Conservation and Nuclear Safety,
Ahrstraße 20, D-53175 Bonn
Dr. Volker Franzius, Federal Environmental Agency,
Bismarckplatz 1, D-14193 Berlin

Summary
Contaminated sites are the legacy of nearly 150 years of industrialisation in Germany. The expected 240,000 suspected contaminated sites which can cause hazards to human beings and the environment are a result of a carefree handling of wastes and dangerous substances. The Federal Laender have the competence for the execution of registration, assessment and remediation of contaminated sites. According to the German Constitution the Federal Government has the concurrent legislative competence on this issue. To avoid different assessment criteria and standards, the Federal Government was preparing a nationwide Act on Soil Protection and Remediation of Contaminated sites which recently passed Parliament and will come into force in March 1999. The country session Germany gives an overview on the problem and dimension of contaminated sites and covers new approades on derelict land recycling as well as financing procedures and R & D-issues. Northrhine-Westphalia will represent the contaminated sites management as an example of the Federal Laender.

The following topics will be pesented:
Framework for contaminated site management in Germany
Andreas Bieber, Dr. Volker Franzius, Dr. Karin Freier

Military contaminated sites
Bert-Axel Szelinski

Requirements for contaminated sites cleanup within the frame work of derelict land recycling
Dr. Karin Freier, Silvia Reppe

Financing clean up of contaminated sites in the new Federal States
Dr. Joachim Sanden

Contaminated sites remediation in Northrhine-Westphalia *
Wolf-Dietrich Bertges

Research and development on remediation technologies
Dr. Karl-Heinz Hübenthal, Uwe Wittmann

Testing facility for groundwater and soil remediation (VEGAS)
Dr. Peter Koschitzky

Research activies of the UFZ Leipzig *
Dr. Ulrich Stottmeister

* Abstracts are not available yet

Contaminated Soil '98, Thomas Telford, London, 1998, 1233

Framework for Contaminated Sites Management in Germany

Andreas Bieber, Federal Ministry for the Environment, Nature Conservation and Nuclear Safety, Ahrstraße 20, D-53175 Bonn
Dr. Volker Franzius, Dr. Karin Freier, Federal Environmental Agency, Bismarckplatz 1, D-14193 Berlin

Competence

According to the German Constitution the Federal States have the competence for the remediation of contaminated sites and groundwater. They have to ensure, that suspected contaminates sites are registered, that the possibly emanating risks are assessed and that necessary remediation is carried out. And they have to meet the expenses for these steps, if someone responsible can not be found.

Extent of the Problem of Contaminated Sites in Germany

At the end of 1997 more that 190,000 sites were registered as being suspected to be contaminated. The registration is mainly focused on sites where waste has been handled or disposed (87,559) and sites where hazardous substances have been handled (103,330). It is estimated, that the number will still increase up to 240,000 sites.

In addition to the contaminated sites of „civil use" origin, Germany is confronted with the warfare related sites and with the contaminated former military sites. The total area that is actually or was formerly used for military purposes is around one million hectares (2.8 % of the area of Germany).
Also armament production sites represent a problem of concern in Germany. An inventory of suspected armament production sites was started in 1990. A rough assessment of the registered 3,240 sites indicates approx. 1,500 hazardous sites.

Federal Legislation

The 190,000 sites being registered as suspected contaminates sites have to be investigated and assessed. These steps should be guided by uniform criteria in order to guarantee a certain comparability. The Federal Soil Protection Act which recently passed legislation and will come into force in spring 1999 and the accompanying sublegal regulations will provide these uniform criteria.
The Federal Soil Protection Act integrates the preventive and the repairing soil protection. The basic idea is the protection from harmful changes in soil. Such changes are given

- when the natural or economic soil functions are impaired and
- when this leads to danger, to considerable drawbacks or nuisance for individual persons or for the general public.

Contaminated Soil '98, Thomas Telford, London, 1998, 1235–1236

Contaminated sites are defined as

- abandoned waste disposal sites (closed-down waste disposal plants or other estates where waste has been treated, stored or disposed) and
- abandoned industrial sites (estates of closed-down plants or other estates where environmentally hazardous substances have been handled)

which cause harmful changes in soil or other hazards for the individual or for the general public.

Soil Quality Criteria

The act on soil protection provides three categories of soil quality criteria inform of soil levels:

- „action levels" indicating as a rule a hazard which has to be warded off; further investigations to ascertain the hazard are usually not necessary;
- „trigger levels" indicating further investigations to ascertain (verify/falsify) whether the soil contamination implies a hazard;
- „precaution levels" indicating a certain chance of future soil problems which need to be addressed in order to avert upcoming damages.

The action levels and the trigger levels are related to the use of the respective site; the decision whether the soil contamination implies a hazard has to take into account how the site is actually used and what future use can reasonably be expected.
Methods for sampling and analysing are defined together with the soil levels.

Technologies and Capacities

As the Federal States (Länder) and the local communities are responsible for the remediation there is no nationwide overview on used technologies available. In 1996 an evaluation for the Federal State of Northrhine-Westphalia on the applied technologies indicated that there is a significant trend towards containment techniques. From 660 applied remedial measures at 498 industrial sites 50 % were excavation measures with subsequent disposal of the soil, 32 % decontamination measures including pump and treat of groundwater and soil vapour extraction technique, and 18 % containment measures. Actual soil clean-up technologies (thermal treatment, soil washing, biological treatment) were 5 %.
Due to the economical situation of the communities there is a common trend rather to use low cost technologies (containment, disposal) than more expensive decontamination technologies.

Contaminated soils are mostly treated off site in stationary treatment facilities. As of October 1997 107 soil treatment facilities with a treatment capacity of 3.8 million t/y are available in Germany:

- 4 thermal treatment facilities (total capacity 168,000 t/y)
- 24 soil washing facilities (total capacity 1.5 million t/y)
- 81 biological treatment facilities (total capacity 2.0 million t/y).

In 1996 the total soil treatment capacity was about 3.4 million t/y; the average used capacity was about 64 %. 56 % of the soil was treated by biological techniques; 39 % by soil washing and only 5 % by thermal treatment.

Contaminated Military Sites

German Experiences

Bert-Axel Szelinski
Federal Ministry for the Environment, Nature Conservation and Nuclear Safety,
Schiffbauerdamm 15, D-10044 Berlin - Phone +49-30 28550-4270 - Fax: +49 30 28550 4375 -
e-mail: wa17a001@WP-Gate.BMU.De

The State of Site Assessment and Clean-up at Military Sites

After reunification Germany was faced with the immense task of managing Soviet military sites while and after the military forces were withdrawn. The process of détente resulting from the dissolution of the Soviet Union led to the closure of more military sites used by the German armed forces and by the NATO allies. This process will be ongoing in the future.

The extent of this task is illustrated by the following figures. To date, a total of 16,179 sites have been handed over by the military to the Federal Finance Administration as owner of the Federal property, covering an area of 371,099 hectares. These figures include 429 garrisons or barracks, 169 larger training areas, 37 airfields and a high number of smaller military property.

The magnitude of the problem and the relatively short time period during which the Soviet troops were withdrawn required the development of a management system to ensure that all relevant sites could undergo a unified, comprehensive assessment of environmental problems.

The comprehensive system to register, investigate, asses, and clean-up the sites left by the Soviet troops consists of the following subsystems[i]:

- Residual Pollution Data Information System (ALADIN)
- Model for the Initial Assessment of Suspected Residual Pollution Areas (MEMURA)
- Model for the Risk Assessment of Military and Armament Contaminated Sites (MAGMA) and the
- System for Cost Assessment for Clean-up of Contaminated Sites (KOSAL).

The creation and application of these systems to the sites formerly occupied by the Soviet troops alone cost about 100 million DM. However, the use of this approach is regarded as being a big money-saver compared to the cost that would have occurred with a site-specific approach. The system is designed to guarantee uniform management. It also provides a basis for a sound priority setting. The experience using the system has been overall very positive. It is now used in a slightly modified form for all other military sites, also.

The assessment of a problem does not automatically mean that it is solved. The remediation of former military sites in Germany is an ongoing process that will still continue for the years to come. Due to serious financial constraints most of the sites that require further investigation and possibly subsequent clean-up have not yet passed the stage of phase II with the detailed investigation of the contamination. Only very few sites, most of them still used by the German military, are undergoing active clean-up.

The new Soil Protection Act which was adopted in February 1998[ii] and regulations prepared under it will be fully applicable for contaminated military sites. This may put additional pressure to proceed with site clean-up.

Although only very few contaminated military sites (about 1-1.5 % of all sites which have been investigated) have been subject to active long-term remedial action,

Contaminated Soil '98, Thomas Telford, London, 1998, 1237–1239

many sources of contamination have been removed in the phase of site assessment by means of immediate actions whenever there was an acute threat to the environment and the public at large.

Most problems are connected to munitions, left or buried on these sites, and pollution from hydrocarbons and the like, particularly at airfields, tank-farms and filling stations. Although most storage tanks have been removed in special programs, only in a limited number of cases the soil and ground water pollution was cleaned-up. The risk of ground water pollution in many of the sites is relatively high. About one third of the sites are situated in water protection areas, two thirds of the sites may be regarded as potentially threatening such areas.

The Reuse of Contaminated Military Sites

With the closure of so many military sites the reuse of such sites is an important issue. There is a lack of a clear-cut *reuse policy* which, however, is difficult to develop since the sites have comparatively different potentials for reuse.

It is the policy of the Federal Ministry for Finance to sell as many sites as possible in the shortest possible time to private investors. The clean-up of the sites is a prerequisite for sales, since the new owner would have to bear the risk of pollution from the sites and may be obliged to clean-up at his own cost. Therefore sales contracts generally provide a clause allowing for price reductions for *necessary* clean-up cost arising in a fixed period after the sale.

Sales of former military properties work rather well in congested areas where there is demand for housing and industrial estates. The sales situation regarding sites like training areas and airfields situated „out in the middle of nowhere", however, is different. In these cases often a commercial reuse is not possible. Some of the Eastern German States therefore have developed programs for using such sites as nature reserves. Very often, particularly where unexploded ordinance poses a threat to the public, fencing of property to keep people away is still common practice.

The discussion on the reuse of sites for which there is no demand has not yet fully started. The Ministry for the Environment has contracted out a small study on the socio-economic aspects governing reuse activities[iii]

Future Developments

Existing clean-up technology has proved to be extremely costly, time consuming and often guarantees only limited certainty of success. This and the application of the Soil Protection Act requires a review of the used clean-up methods also considering the cost-benefit relation .

Research and development activities have been focused on this. A program assessing remediation at tank farms will be concluded this year. It is designed to compare different remediation technologies, their success and the cost involved. It will also give recommendations how to deal with the site specific problems of tank farms of the military in the future. The results of this study will be presented to the interested public for discussion in mid 1998.

Due to the existing financial restraints the „intrinsic remediation" by „natural attenuation" has become subject of controversial discussion also in Germany. Although the *phenomenon* of „natural attenuation" is well known and established for almost 50 years, the practical use of it is restricted due to a substantial lack of knowledge which does not allow predictions on how it would work in practice on concrete problematic sites.

There is, however, general agreement that it would be an inexcusable mistake to disregard natural attenuation in cleaning-up sites. Germany is in a particularly favorable condition, as the legal conditions allow a *risk oriented approach*[iv]. This would in principle allow to make use of natural processes when it can be established that this would not create additional risks. However, a *wait and see philosophy* would be totally unacceptable if the behavior of the pollutants cannot be predicted in a scientifically sound manner and unless the pollution is carefully monitored. Since there is no sufficient operating history to use the *mechanisms* of intrinsic remediation research will have to fill the existing gaps in knowledge.

It is no coincidence that intrinsic remediation is of particular interest for military contaminated sites. First of all most larger military facilities are situated far from congested areas, thus reducing the risk for the public. Secondly there is only a limited number of pollutants present at military sites of which hydrocarbons and related substances are the most common. Mineral oils and fuels can be biodegraded. The rate and time in which bio-degradation takes place in given environmental conditions can only be assessed in a very extensive process requiring thorough monitoring and the development of individual modeling schemes. Generally applicable standards to make use of intrinsic remediation are not available in Germany. It is therefore planned to start a research program to i.a. find answers to the following questions:

- What is the influence of the *concrete* natural conditions, i.e. properties of the medium and transport of pollutants vs. Degradation rate ?
- What are the *process products,* are there metabolic reactions, and is there a transformation into other substances which may be even more hazardous than the original contaminant itself?
- Where are the limits to consider the use of intrinsic remediation as a *tool* ?
- What are the substances other than mineral oils and other hydrocarbons on which this „method" can be used ?

Only if these questions can be positively answered intrinsic remediation can be considered in Germany as an applicable means that can be used for the clean-up of contaminated military sites. A four year research program will start this year to find answers to the first three of these questions.

References:

---

[i] The system is described in detail in the final documentation *Determination of Suspected Residual Load Areas on the Properties of the West Group of Soviet Troops;* IABGmbH, Ottobrunn, 1995

[ii] **Bundesbodenschutzgesetz** (Federal Soil Protection Act) passed on February 6, 1998 (not yet published)

[iii] Study: *Reusing Former Military Lands,* executed on behalf of the Ministry for the Environment; IABGmbH and the Bonn International Center for Conversion, Bonn, 1997

[iv] In the United States the problem how to fit *intrinsic remediation* in the existing legal framework is still unsolved. However, important work has been done to develop guidelines. Cf. American Society for Testing and Materials, *Standard Guide for Risk-based Corrective Action Applied at Petroleum-Release Sites;* ASTM: West Conshohocken, PA, 1995 (E1739-95)

Requirements for Contaminated Sites Cleanup within the Framework of Derelict Land Recycling

Dr. Karin Freier and Silvia Reppe
Federal Environmental Agency, Bismarckplatz 1, D - 14193 Berlin

Land consumption in the Federal Republic of Germany amounts to 80 to 120 hectares/day. This figure is contrasted by around 20,000 hectares of derelict industrial sites in inner cities, which could be re-used if appropriate evaluation standards and criteria were to be established for this purpose. This has prompted the Abandoned Contaminated Sites Section of the Federal Environmental Agency to initiate an R+D project entitled "Requirements for Contaminated Sites Cleanup within the Framework of Derelict Land Recycling", which commenced on 1 September 1997 and whose results are expected to be available by 30 June 1999.

By means of selected case studies, requirements are to be formulated to supplement those laid down in the police law and the special legislation of the individual federal *Länder*, the regulations to be issued under the Federal Soil Protection Act and the provisions governing urban land use planning. In addition, technical and legal shortcomings which impede an effective recycling of derelict land are to be identified.

The contractors are the Tendering Group of the Central Soil Decontamination Department of Deutsche Bahn AG as well as the Gesellschaft für Projektmanagement und Grundstücksentwicklung mbH (GPE) in cooperation with Ruhrkohle Immobilien AG. The above-mentioned Tendering Group is cooperating with the soil laboratory Ahlenbeck, whose task under the project is to deal with general aspects of contaminated sites cleanup as part of derelict land recycling, and the law firm Leinen & Derichs, which is concerned with the analysis of relevant legal aspects. A point of great importance to the project is that, as the owner of numerous derelict industrial sites, the Tendering Group has a major interest of its own in the rapid and practicable implementation of the results of the project and that it is ensuring unlimited access to all data and detailed information available on the sites under investigation, including information on specific financing and legal issues.

A legal definition of the term "derelict land recycling" (in German: *Flächenrecycling)* does not yet exist in Germany. Therefore, the definition given by the ITVA Expert Committee on Derelict Land Recycling was adopted for the purposes of the research project: *"Derelict land recycling means the use-related re-integration of such land into the economic and natural cycle which has lost its previous function or use.... through measures in the fields of planning, environmental technology and economic policy."*

Based on a matrix to be developed in the project, 10 sites that appear most suitable for further research work are to be identified out of a total of 50 supraregional sites of different sectors and sizes. Both negative and positive aspects will play an important role in the assessment, as will all relevant site characteristics. The information compiled is to be used to develop standards for uniform assessment. The 10 case studies will be performed by the engineers' offices which have served the respective projects as consultants.

Contaminated Soil '98, Thomas Telford, London, 1998, 1241–1242

Aspects to be dealt with to achieve the project's objective are the following:

1. Description of effect mechanisms, influencing factors and basic conditions through the analysis of complex projects from derelict land recycling practice.
2. Determination of influencing variables for use by participating parties in decision-making, with the objective of developing sites in an efficient manner.
3. Approaches to the monetary valuation of the relation between site treatment and value creation through site development.
4. Evaluation of the parameters: residual risk - value creation through site development - marketing success.
5. Legal security in the development, treatment and use of the site.

The re-integration of the sites is to be supported by improving their negative image and through the development practice-oriented procedural guidelines. The aim is a subsequent use of the sites at the highest possible quality level.

Financing clean up of contaminated sites in the new Federal States

Dr Joachim Sanden
Federal Ministry for the Environment, Nature Conservation and Nuclear Safety, Ahrstraße 20, D-53048 Bonn, Germany; phone +49-228-305-3412, fax: +49-228-305-2396

After reunification the question of remediating existing contaminated sites was of great significance in the process of privatising industrial enterprises in the new *Länder* (the new states of Mecklenburg-Western Pommerania, Berlin, Brandenburg, Saxony Anhalt, Saxony and Thuringia). Potential investors were rarely prepared to accept the risk of having to pay for clean-up-measures arising from the take over of plants and, in many cases, preferred to build new factories on greenfield sites.

To counteract this trend legal provision was made - applicable for a transitional period - for exempting investors from having to bear the costs of remediating the environmental damage they encounter on polluted sites. According to the so called „exemption clause" of the Unification Treaty, investors in the new Federal States, who acquire installations used for commercial purposes, or within the framework of economic untertakings, are not liable for any damage caused prior to 1 July 1990 as a result of the operation of the installation. Exemptions may be granted after the interests of the purchaser, the general public and environmental protection have been weighted. Liability due to claims based on civil law remains unaffected.

The Federal Government and the *Länder* have jointly made a maximum of DM 10 billion available to fund the necessary clean-up work. According to the „Administrative Agreement for Financing the Clean-up of Contaminated Sites" adopted by the Federal Government and the new Federal States on 22 December 1992, the remediation costs are shared by the Federal Government and by the new *Länder*:

Where former state enterprises are involved, that means the transfer to private partnership, the Federal Government and the respective *Länder* share the costs on a 60:40 basis. A total number of 1 billion DM per year for a period of 10 years are commited for the 60:40 projects.

For a total of 23 large-scale projects, where costs generally exceed DM 100 million, the Federal Government and *Länder* have aggred to meet the costs on a 75:25 basis. The total costs involved are estimated at DM 6.5 billion. These measures are directed above all at sites used for large-scale chemical production, steel production and mining as well as some ship-yards. These projects comprise the highly polluted areas of the chemical industry (the „chemical triangle" of Halle, Leipzig and Bitterfeld), the shipbuilding industry on the Baltic Sea and other „hot spots". For each of these projects a comprehensive remediation concept has to be elaborated.

Another large project already agreed is the clean-up of opencast lignite mines. The Federal Government and *Länder* are providing DM 7.5 billion over the period 1993-1997 for remediation of mining sites in Central Germany and in Lausitz.

Contaminated Soil '98, Thomas Telford, London, 1998, 1243–1244

For the clean-up of the Wismut sites (uranium mining) 13 billion DM have been made available by the Federal Government for the entire project, which will be continue beyond the year 2000. The remediation of the uranium mines of the former Wismut AG company in Thuringia and Saxony represents one of the biggest environmental repair programmes in Germany.

The total public funds available over the next ten years for clean-up in East Germany amount to at least 35 billion DM.

Research and Development: "Contaminated Sites Remediation Technologies"

Dr. K.-H. Hübenthal 1), Dipl.-Ing. U. Wittmann 2)

1) Federal Ministry for Education, Science, Research and Technology (BMBF), Bonn
2) Federal Environmental Agency, Berlin

1. Work objectives and projects funded to date

Since the mid-1970s, the Federal Ministry for Education, Science, Research and Technology (BMBF) has supported the performance of R+D projects in contaminated sites remediation on a major scale. Funds totalling more than DM 400 million have been provided to finance over 300 projects aimed at the development of new methods, processes and technologies. In view of the more than six-fold increase in the number of suspected contaminated sites identified in Germany (from 38,000 in 1983 to an anticipated 240,000 in the year 2000) and the need for action in the new Federal *Länder* (States) in particular, this funding has proved to be appropriate and necessary.

2. Characterisation of selected work results

The projects funded to date were primarily concerned with the development of such scientific and technical solutions as are needed to reliably detect contaminants in soil and to remove them from the soil in a cost-effective manner or at least interrupt contaminant transfer to human beings. They are to ensure that groundwater deposits are no longer put at risk and that valuable building land in industrial regions and towns can be used safely.

Thus, for example, the research projects carried out up to the late 1980s on the containment of the Georgswerder and Gerolsheim landfills resulted in a multitude of solutions for the immobilisation of pollutants and the isolation of contamination "hot spots" by means of slurry walls and surface sealing systems.

As a result of the development of thermal, chemical, physical and biological soil cleaning methods, likewise funded by the BMBF as from 1985, soil cleaning services have been offered on the market since 1990 for salts, acids, alkalis, mineral oil, solvents, aromatics, and toxic heavy metals.

As a prerequisite for a more reliable and cost-effective identification of barrier-forming soil properties, geophysical, geochemical and hydrogeological exploration methods have been tested and developed further at 7 sites since 1990 under the direction of the Federal Institute for Geosciences and Natural Resources. The results of this research project consisting of 28 sub-projects and entitled "Methods for the exploration and

description of soil at landfills and contaminated sites" is currently being published at Springer-Verlag as a 6-volume compendium.

In order to improve possibilities for evaluating and advancing cost-effective in-situ remediation techniques under nearly natural conditions, support was provided for the establishment of an experimental plant for groundwater rehabilitation and contaminated sites cleanup ("Versuchsanlage für Grundwasser- und Altlastensanierung" - VEGAS) at Stuttgart University. The plant consists of 4 large containers with volumes of between 30 and 790 cubic metres. Put into operation in 1995, the plant's test capacity is now being utilised in large part.

Complementing the development of soil cleaning methods, funding of "model projects in contaminated sites remediation" was started in 1990. The aim of this measure was to test and evaluate the new cleaning techniques on site under the harsh conditions encountered in daily practice, using them separately or in combination. This was to give impetus to the effective use of the techniques developed and generate experience about their behaviour in long-term use and their effectiveness. Many findings of practical relevance were obtained in what was a total of 13 projects. They demonstrated, among other things, the economic and ecological limitations of appropriate combinations of methods. Another insight gained was the limited nature of existing approaches to contaminated sites remediation, which often are confined to the solution of individual problems. Of particular importance are the documented ways of performing cost-effective, environmentally appropriate and use-oriented remedial measures at former chemicals and metals production sites, gasworks and ammunitions manufacturing sites. The results of this funding measure, which is due for completion in 1998, will be published as a compendium.

Based on encouraging results from tests carried out on a laboratory and pilot-plant scale, work is being done to further develop biological soil cleaning methods. They are to be used as a cost-effective and soil-conserving means of destroying organic compounds in particular. These compounds so far could only be removed from soil by means of resource-intensive chemical-physical methods. To develop alternative solutions to these methods, a joint research activity entitled "Biological soil decontamination methods" has been under way since 1994. Consisting of 40 projects, this activity is concerned with exploring the use of bacteria and fungi as well as of ligneous and herbaceous plants for the destruction and removal of such organic compounds as e.g. TNT, hexogen, nitrophenols, aromatic amines, phenols, and dioxins. The methods developed are currently being tested on a commercial scale; this

includes testing for degradation of explosives-typical compounds at the site "Tanne" near Clausthal-Zellerfeld.

Efforts undertaken to rehabilitate contaminated sites in the post-mining landscapes in the new Federal *Länder* include the development of new containment techniques capable of safely isolating deposits of contaminants from chemical plants in this region under extreme conditions. There is, in particular, the need to provide effective sealing systems to a depth of up to 100 metres which are stable for the long term even under acidic groundwater conditions.

3. Future fields of funding

Presented to the public in September 1997, the new Federal Government programme "Research for the Environment" continues to give high priority to research in the field of contaminated sites remediation. The programme's approach, "Shaping the environment at regional level", in particular takes into account that the contaminated sites problem which mainly dates from the last two decades will take several decades to solve. Funding, therefore, will concentrate on research aimed at developing lasting solutions of importance to economic development and regional planning in industrial and municipal agglomerations in e.g. the new Federal *Länder*. Topics emphasised include the development of reactive wall systems and the investigation of natural degradation processes at large sites with low levels of contamination, but also the containment of contaminated sites through contaminant fixation and retrofitting with bottom liner systems.

VEGAS: A research facility for subsurface remediation at the University of Stuttgart and a research framework

Dr.-Ing. Hans-Peter Koschitzky & Dr.-Ing. Baldur Barczewski
Institut für Wasserbau • *VEGAS* • Universität Stuttgart • Pfaffenwaldring 61 • D-70550 Stuttgart
phone +49-711-685-4717/14 • fax: +49-711-685-7020 • e-mail: vegas@iws.uni-stuttgart.de

The Research Facility *VEGAS* (Versuchseinrichtung zur Grundwasser- und Altlastensanierung) at the University of Stuttgart, Germany, is in full operation since fall 1995. The facility includes large-scale experimental containers of various sizes with volumes up to 850 m^3. In contrast to field investigations at contaminated sites, experiments in *VEGAS* are conducted under controlled and reproducible conditions, therefore mass balances and remediation efficiencies can be determined. The large test containers allow investigations of realistic 3-D subsurface structures which take aspects of natural spatial variability into consideration. Investigations which combine field and laboratory experiments with *VEGAS* technical scale experiments are highly encouraged bridging the gap between small-scale laboratory experiments and large-scale field investigations (upscaling).

The *VEGAS* hall is located at the Institut für Wasserbau, Lehrstuhl für Hydraulik und Grundwasser (Institute of Hydraulic Engineering, Chair of Hydraulics and Groundwater). It is equipped with several technical installations (high-voltage current, compressed air, nitrogen and water in- and outlets etc.). A water treatment plant for organic and anorganic contaminants has been installed to clean up contaminated water from the test set-ups.

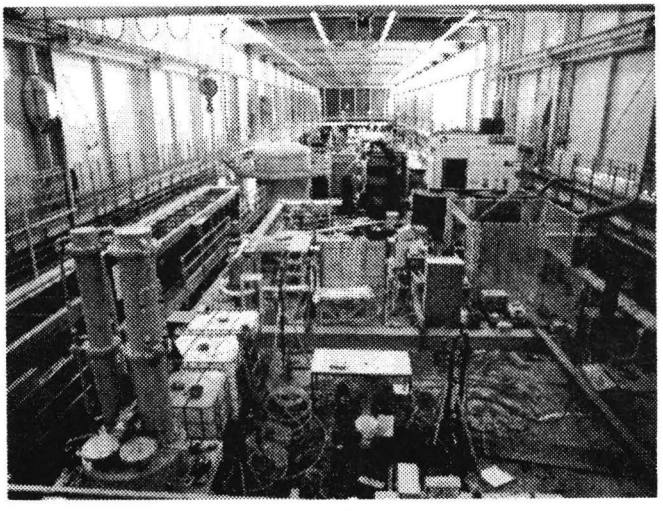
For the experimental *VEGAS* projects various large scale containers are available: a *large rectangular container* (19.5m x 9m x 4.5m) with removable walls dividing the container into 3 compartments (9m x 6.2m x 4.5m); two *transportable containers* (6.5m x 2.2m x 2.5m) that can be filled with contaminated soil at actual spill sites and transported with trucks to *VEGAS*; a *long flume* (16m x 1m x 3m) with a side-wall made of glas to allow visual observation of the experiment; a *cylindrical container*, (diameter 3m, height 6m); a *closed flume* (10m x 0.2m x 0.7m) for tests under anaerobic conditions. All containers are made of stainless steel and are accessible from all sides. Thus any leakage can be detected immediately, and installation of additional equipment is possible.

In addition, the following laboratories and workrooms are available: a *climate control room* with a temperature range of +4°C to +30°C, a *room with an explosion shelter* for experiments with highly combustible substances and explosive materials (e.g. light gas), a *special storage room* for contaminated samples and materials, a *state-of-the-art chemistry laboratory* for on-site analyses with rooms for sample preparation and instrumental analyses and *measuring and electronic laboratories*.

Organization: The regulations governing the basic organization of *VEGAS* were agreed upon by the University of Stuttgart, the Ministry of the Environment of the state of Baden-Württemberg and the Federal Ministry for Science, Education,

Contaminated Soil '98, Thomas Telford, London, 1998, 1249–1252

Research and Technology. An advisory council (Beirat) regulates the topics and priorities of *VEGAS* research. It consists of representatives from each of the above-mentioned institutions as well as *VEGAS* management staff and independent representatives from science, research and industry.



View into the VEGAS facility

VEGAS offers research opportunities for developments on in-situ subsurface remediation to industry, universities and research institutions throughout the country as well as for cooperation partners abroad. Every project is responsible for its own funding. In general the experiments will be carried out by the researcher, assisted by staff of *VEGAS* if necessary.

The Objectives of *VEGAS* is to test and optimize existing techniques and to develop new techniques for in-situ remediation of contaminated aquifers and soils. *VEGAS* focusses also on evaluating methods for monitoring the mobility of contaminants in the subsurface and improving the assessment of contaminated sites. Improvements of methods for determining the overall mass and distribution of contaminants in the subsurface and techniques for identifying physical and chemical subsurface properties are being developed as well. In addition to the technological developments, experiments deal with the investigation of the behavior of contaminants in the subsurface. Physical experiments are coupled with numerical simulations in order to improve the quantitative understanding of the relevant processes.

Research Topics Interpretation of the numerous complex processes which occur simultaneously during remediation requires the cooperation of representatives and groups from various disciplines. Most of the *VEGAS* projects are interdisciplinary efforts. For the first research phase in *VEGAS,* **five main research topics** and several individual projects have been established. *VEGAS* is open to new project proposals in line with the objective of the facility.Regular symposiums and workshops are scheduled to report on research results and facilitate transfer of the developing technologies towards practical application.

Optimization and further development of hydraulic remediation techniques: In general in-situ extraction processes are based on forcing energy, chemicals and fluids through the subsurface in order to dissolve the contaminants and pump them out.

Problems are caused by the high variability of the hydraulic conductivity, the difficult accessibility of zones with low permeability, the low solubility of some contaminants and low mass-transfer rates.

Several methods for increasing the extraction efficiency will be tested, i.e. arran gements with one to five vertical circulation wells, recirculation wells some with air sparging inside the wells for the clean-up of volatile ground water contaminants as well as the use of hydraulic systems with the application of biodegradable surfactants.

Non-aqueous phase liquids (NAPL) in the vadose zone: Since non-aqueous phase liquids (NAPL) with pore-saturations of less than 10-30% cannot flow in the subsurface, contaminant spills with NAPL's pose a unique problem for in-situ remediation. They exist as a long-term contaminant source for soil vapor, soil water and ground water. The remediation of contaminated sites with the traditional pump and treat (water and air) techniques are mostly inefficient because the mass transfer is limited by the solubility, the desorption and the evaporation pressure of the contaminants. A precondition for conducting quantitative experiments is the availability of suitable methods for in-situ determination of contaminant contents, as well as the knowledge of the relationships between capillary pressure and saturation. Suitable numerical simulation methods for multiphase flow and transport in the subsurface have to be developed using the results of the large-scale experiments.

The objective of the research work is to improve existing techniques and to develop new ones for in-situ remediation of NAPL-spills. Basic investigations on multi-phase behavior of NAPL's in the subsurface are conducted, as well as technology-oriented experiments involving the injection of heat (steam injection) to mobilize the contaminants.

Improvement of the remediation efficiency of soils contaminated with PAH's: Former gasworks present a major contamination problem in Germany. The soil on most of these sites is polluted with coal tar and its components which leads to groundwater contamination through mobilization of polycyclic aromatic hydrocarbons (PAH's) running off the residual tar phase.

The use of permeable reactive sorption barrier in the downstream of a residual source presents a new in-situ technology. The contaminant is effectively retained in the sorption barrier, where the contaminants are transformed by PAH degrading bacteria (bioactive sorption barrier).

Anerobic, microbial contaminant transformation for in-situ remediation of contaminated soils and aquifers: Chlorinated ethenes (e.g. PCE) belong to the most frequently occurring contaminants in soil and groundwater. They are characterized by a high toxic potential and a high mobility. In laboraty experiments it has been shown that perchlorothene can be completely dechlorinated under anaerobic conditions. In field applications, however, the degradation process often leads to dichloroethylene and vinylchloride, a known cancerogen.

The objective of an interdisciplinary research project is to determine optimal conditions for complete microbial dechlorination of PCE, i.e. type and concentration of co-substrates, redox potential and pH, and to investigate how these conditions can be realized in a large-scale 2-D model aquifer with spatially variable soil properties.

Interactions between bio-transformations, mass-transfer and advective dispersive transport are to be identified and quantified.

Immobilization-, containment- and biochemical degradation techniques: Inorganic contaminants can be immobilized in the subsurface by changing the physicochemical environment, especially the pH and the redox potential by adding reactive substances in large quantities at low costs. Several projects investigate the long-term stability of immobilized contaminants and the influence of heterogeneities, of other contaminants and of the natural geochemical factors on immobilization reactions.

Other long-term remediation methods are reactive and sorptive walls. The contaminated groundwater stream is led through permeable reactive walls (funnel and gate) where the contaminant is fixed and degraded. To optimize the long-term reactivity further investigations on the influence of inorganic and organic material that might inhibit degradation reactions in the groundwater are needed. In one of the projects the factors which limit reductive dechlorination of volatile chlorinated organic hydrocarbons in reactive walls containing Fe°-particles is investigated under different physicochemical and hydraulic conditions.

Further research topics within the VEGAS program framework: In addition to the main topics outlined, various aspects of subsurface contamination and remediation problems are investigated. These include for example projects on: in-situ soil homogenization by mechanical and hydraulic methods; development of in-situ technologies for microbiological remediation for several contaminats; investigations of geophysical properties of contaminated soils; Natural attenuation of PAH's in aquifers.

Participating institutions and cooperations: Many research institutions and industrial companies are currently involved in the research program of *VEGAS*, at the moment about 20 institutes from universities, 6 research institutions, mor than 10 industrial companies and engineering consultants and 5 Authorities. Several international institutions cooperates with *VEGAS*.

Acknowledgement: We greatfully acknowledge the funding for *VEGAS* by the German Federal Ministry of Education, Science, Research and Technology (BMBF) and the Ministry of the Environment of Baden-Württemberg. We wish to thank all annonymous services foe their highly constructive suggestions.

References

Barczewski, B.; Koschitzky, H.-P. (1996): *The VEGAS-Research Facility: Technical Equipment an Research Projects*, in: H. Kobus, B. Barczewski, H.-P. Koschitzky (eds.): *Groundwater and Subsurface Remedation, Research Strategies for In-situ Technologies*, ISBN 3-540-60916-4, Springer Verlag, Berlin-Heidelberg, S. 129-157

Kobus, H. (1996): *The Role of Large-Scale Experiments in Groundwater and Subsurface Remediation Research: The VEGAS-Concept and Approach*, in: H. Kobus, B. Barczewski, H.-P. Koschitzky (eds.): *Groundwater and Subsurface Remedation, Research Strategies for In-situ Technologies*, ISBN 3-540-60916-4, Springer Verlag, Berlin-Heidelberg, 1996, S. 129-157

SOIL POLLUTION PREVENTION AND CONTAMINATED SITE MANAGEMENT IN SWITZERLAND

C. Wenger[1], J. Dettwiler[1], R. Philipp[2], Ph. Vallat[3], C. Munz[4], A. Kyas[5], M. Jaggy[6]

[1] *Swiss Agency for Environment, Forests and Landscape, CH-3003 Bern, Switzerland*

[2] *SC+P Sieber Cassina + Partner AG, Langstrasse 149, CH-8004 Zurich, Switzerland*

[3] *Federal Department of Defence, Civil Protection and Sports DDPS, General Secretariat, CH-3003 Bern, Switzerland*

[4] *BMG Engineering AG, Ifangstrasse 11, CH-8952 Schlieren, Switzerland*

[5] *UBS Union Bank of Switzerland, Environment Desk Corporate Banking, P.O.Box, CH-8021 Zurich, Switzerland*

[6] *Swiss Federal Institute for Environmental Science and Technology EAWAG, Ueberlandstrasse 133, CH-8600 Dübendorf, Switzerland*

Key words: Legislation, contaminated sites, soil protection, register, military sites, risk assessment, intervention values for remediation, costs, liability, financial aspects.

SUMMARY

Legislation on the prevention of soil pollution exists in Switzerland since the early eighties and is actually completed with trigger and clean-up values and measures against physical impacts on soil. The registration and evaluation of about 50'000 suspected sites as well as the remediation of the estimated 4000 contaminated sites is regulated in a new *Ordinance on to the remediation of contaminated sites*. The estimated overall costs of more than 3 billion ECU have to be beared by the polluters or by a Federal funding for the remediation of orphan sites and landfills.

KURZFASSUNG

Rechtserlasse zur Vermeidung von Bodenbelastungen existieren in der Schweiz seit den frühen 80-ern. Sie werden momentan ergänzt durch Prüf- und Sanierungswerte sowie Massnahmen im physikalischen Bodenschutz. Die Erfassung und Untersuchung von ca. 50'000 Verdachtsstandorten sowie die Sanierung von vermutlich 4000 Altlasten soll mit der neuen Altlasten-Verordnung klar geregelt werden. Die Gesamtkosten von mehr als 3 Milliarden ECU müssen von den Verursachern oder einem Bundesfonds für die Sanierung von herrenlosen Altlasten und Altdeponien getragen werden.

RESUME

Des textes législatifs relatifs à la réduction préventive des atteintes portées au sol par des substances nocives existent en Suisse depuis le début des années quatre-vingts. Ils sont actuellement complétés avec des valeurs d'appréciation et d'assainissement ainsi que par des mesures contre les impacts physiques sur le sol. Le recensement et l'analyse d'environ 50'000 sites suspects et l'assainissement des 4000 sites contaminés estimés seront réglés dans la nouvelle ordonnance sur les sites contaminés. La totalité des frais, qui s'élèvera à plus de 3 milliards d'Ecus, doit être supportée soit par les pollueurs, soit, lorsqu'ils ne peuvent être identifiés ou s'il s'agit d'une ancienne décharge, par un fond fédéral pour l'assainissement des sites contaminés.

Contaminated Soil '98, Thomas Telford, London, 1998, 1253–1262

1. INTRODUCTION (C. Wenger)

The population of Switzerland is about 7 million, living in an area of 41'000 km^2. Outside the sparsely populated mountainous region, which comprises about 60% of the country's surface, most people live or work in the urban areas of the lowland. The country's political structure is federalist, organised and divided into 23 states, called Cantons. These Cantons are very different in terms of surface area and population, as well as economy, industrialisation and scientific background. Therefore also the industrial waste, waste managment and the environmental impacts, vary considerably.

The first steps towrads a systematic assessment and remediation of contaminated sites were made by local authorities in 1985. Today about 75% of the estimated 50'000 suspected sites are registered by the Cantons and the Federal Department of Defence and up to 200 contaminated sites have been remediated to date. According to current experience 5-10% of the polluted sites need to be remediated. The overall remediation costs for these contaminated sites are estimated by the Federal Agency at over 3 billion ECU.

2. THE SWISS LEGISLATION ON PREVENTION OF SOIL POLLUTION (J. Dettwiler)

2.1. The Law of 1983 relating to the Protection of the Environment *(amended in 1995)*

Federal legislation in environmental pollution protection in Switzerland was first introduced in 1983. Independently, however, a Federal Law on the protection of waters has been in force since the mid-fifties, and has been amended several times. Spatial planning and economic use of soils (land) is the subject of yet another law - independent of the two previously mentioned.

The purpose of the *Federal Law of 1983 relating to the Protection of the Environment* is to protect persons, animals and plants, their biological communities and habitats against harmful effects or nuisances and to maintain the fertility of the soil. Soil pollution means the physical, chemical and biological modification of the natural composition of the soil, while soil means the unsealed top layer of land where plants can grow. This covers the top layers in the *A-horizon* of soils as well as most of the underlying *B-horizon* - all of the *C-horizon* being excluded from soil protection measures.

Swiss soil protection policies and contaminated sites remediation measures are dealt with separately. This legal framework is the consequence of a specific political decision in parliament:

- **The protection of soil quality is precautionary** and with a view to preserving soil fertility in the long term *(see: Amendment to the Federal Ordinance on Soil Quality, 1998 - in preparation).*
- **Remediation of contaminated sites** is a very costly curative measure for repairing actual environmental effects caused by serious soil contamination occurring on specific sites *(see: Federal Ordinance relating to the remediation of polluted sites, 1998 - in preparation).*

2.2. Specific measures to protect the soil

For the long-term preservation of soil fertility, measures against chemical and biological soil pollution are laid down in the implementing regulations on the Laws relating to Water Pollution Control of 24 January 1991, on Disaster Prevention, on Air Pollution Control, on Environmentally Hazardous Substances and Organisms, and on Waste and Incentive taxes. Soil protection is thus carried out at the place of emissions, and not in the soil itself.

Furthermore the soil may be physically affected only to the extent that its fertility is not permanently degraded; this should not apply to land used for building. The Federal Council may issue regulations or recommendations on measures against physical impacts, such as erosion or compaction.

Environmental protection in Switzerland is implemented by the enforcing cantonal authorities (Cantons) by means of emission controls, e.g. in the areas of waste managment, hazardous substances and air pollution control. Implementation thus is not at Federal Government level, but assigned to the enforcing cantonal authorities, as these are closer to the actual environmental problems in question. The Federal Government provides data on soil quality (chemical criteria) from its own countrywide monitoring network, *NABO*.

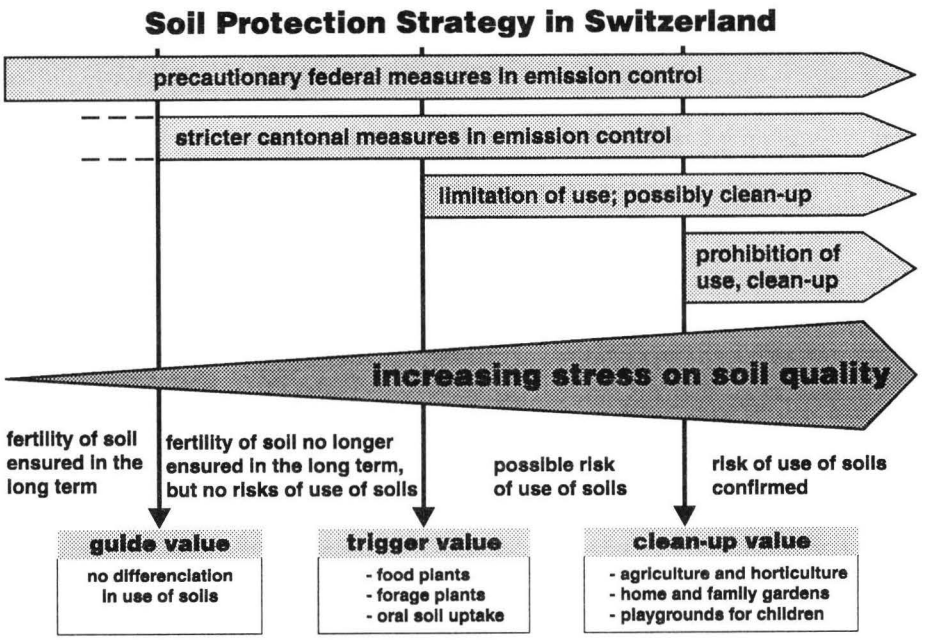
If soil fertility in certain areas cannot be guaranteed in the long term, the Cantons, in agreement with the Federal Council, can introduce as necessary stricter regulations on requirements for sewage infiltration, limitation of emissions for installations, the use of substances (e.g. fertilizers and pesticides), and the effect of organisms or other physical factors on soil.

If the soil pollution endangers humans, animals or plants, the Cantons can restrict the use of the soil as far as necessary. Soil is normally used for horticulture, agriculture or silviculture. If normal cultivaation is impossible in a specific location without endangering humans, animals or plants, the Cantons will enact measures to reduce the soil pollution at least to the extent that a non-hazardous cultivation is possible.

Finally, the Federal Government of Switzerland (Federal Council) may set *guide values* and soil *remediation values* (*"clean-up"* values) for assessing the pollution of the soil:

- The **guide values** indicate the pollution level above which, in the light of current scientific knowledge or experience, soil fertility is no longer guaranteed in the long term.
- The soil **remediation values** indicate the pollution level above which, in the light of current scientific knowledge or experience, certain uses are not possible without endangering humans, animals or plants.

The technical measures are laid down in the *Ordinance of 1986 relating to pollutants in soil (in revision 1998).*



3. THE LEGAL FRAMEWORK FOR THE MANAGEMENT OF CONTAMINATED SITES IN SWITZERLAND (C. Wenger)

3.1. Regulations for contaminated site management in the 1995 revised Law relating to the Protection of the Environment

The amendment to the Law of 1983 relating to the Protection of the Environment regulates the management of contaminated sites for the first time in Swiss environmental legislation, in the following three articles:

- **Registration and remediation**: Obligation for the registration of landfills and other sites polluted by waste (contaminated sites) in a register open to the public; obligation to remediate polluted sites, if they result in harmful effects or cause a nuisance to the environment or if there is a danger that such efects may arise (contaminated sites).
- **Regulation of financing**: "polluter pays" principle; the owner of a site is excepted if he or she could not have had any knowledge of the contamination, he or she did not stand to gain from the contamination, or will not stand to gain from the remediation. The authorities rule on the division of the costs if those with a remediation obligation so require.
- **Levy to fund remediation**: levy on landfills of up to 20% of the average costs in order to finance remediation projects, where the polluter cannot be identified or cannot pay, or where domestic waste is to be remediated.

3.2. Objectives of the Ordinance relating to the remediation of contaminated sites

Based on the revised Law relating to the protection of the environment the Ministry of Environment, Traffic, Energy and Communication plans to put into force the Ordinance relating to the remediation of contaminated sites by 1 July 1998. This ordinance has the following objectives:

- **stop emissions at source:** the remediation criteria are not based on the pollution itself but on the emissions from it, that lead to unacceptable immissions in waters, air or soil; decontamination, containment and use-restrictions for the soil are all therefore acceptable as remediation measures;
- **cooperation between polluters and authorities:** authorities and polluters may carry on working as long as possible under agreements, instead of the need for a ruling; agreements among branches of industry should be encouraged;
- **legal equality** through harmonized criteria (e.g. 72 intervention values, remediation targets, leachate tests) and uniform requirements for the elaboration and management of registers, planning and execution of investigations, as well as monitoring and remediation projects;
- **prevention against new risks:** building activities on polluted sites are permitted only if it can be proved that the site does not need remediation, or if the project does not hinder future remediation, or if it will be remediated in the course of the project; containment measures have to be effective long-term, controllable, reparable and financially guaranteed.

3.3. Priority setting and stepwise management

1. **Registration and prioritization:** the register of polluted sites is open to the public and must be completed by the Cantons by the year 2003. The registered sites should be prioritized and the register updated continuously. Sites which are completely decontaminated will be deleted from the register;
2. **remediation decision:** On the basis of a historical and/or technical investigation it will be decided whether the site needs no further action, monitoring is necessary, or remedial action is required (for procedure and criteria see chapter 5);
3. **remediation objectives and urgency:** the general objectives of remediation are to remove the need for remediation; on the basis of the results of the risk assessment the Cantons may deviate from these general objectives under certain circumstances (according to use, ecological and economic commensurability, environmental merit); sites which present an acute danger must be treated immediately, for others the date by which a remediation project is to be completed must be set by the Cantons according to the risk assessment;
4. **remediation:** the polluter is obliged to devise a remediation project which includes remediation and monitoring measures (including waste disposal, long-term feasibility, time needed to reach the objectives), an eco audit of the measures to be taken, preventive measures for the case that the remdediation undertaken fails, cost-effectiveness, distribution of costs, etc..

4. THE REGISTER OF POTENTIALLY CONTAMINATED SITES OF THE FEDERAL DEPARTMENT OF DEFENCE: COSTS AND BENEFITS OF A SYSTEMATIC SITE IDENTIFICATION (R. Philipp, Ph. Vallat)

4.1. Register of potentially contaminated sites: legal bases, aims

One percent of the 41'000 km^2 of Swiss territory is used for military purposes, either for troop exercises or for infrastructure, defence equipment or other military activities. The land areas are seldom used purely for military purposes: often civil activities such as agriculture, tourism, etc. are also carried out to a small extent. Under the revised Envi-

ronmental Protection Law the DDPS is required to establish a register containing contaminated sites and to remediate those which pollute the environment. The aim of the DDPS register of potentially contaminated sites is to include systematically all sites with environmentally relevant activities, and to subdivide them into cases of negligible importance and those which require additional investigation (Fig. 2). The register should serve as a useful planning instrument in DDPS construction projects, as well as during the liquidation (demilitarisation) of military installations.

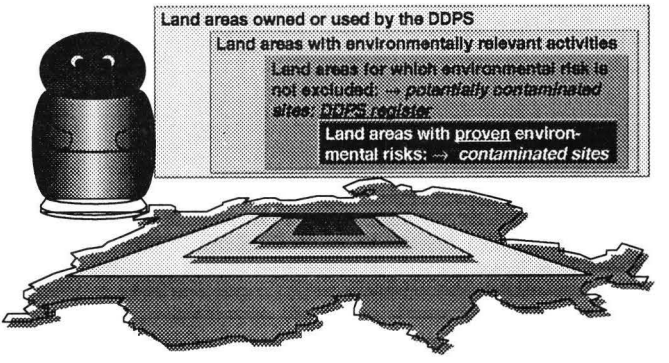


Fig. 2: Elimination of cases of negligible importance, and concentration on sites which necessitate remediation according to the "Babushka doll principle".

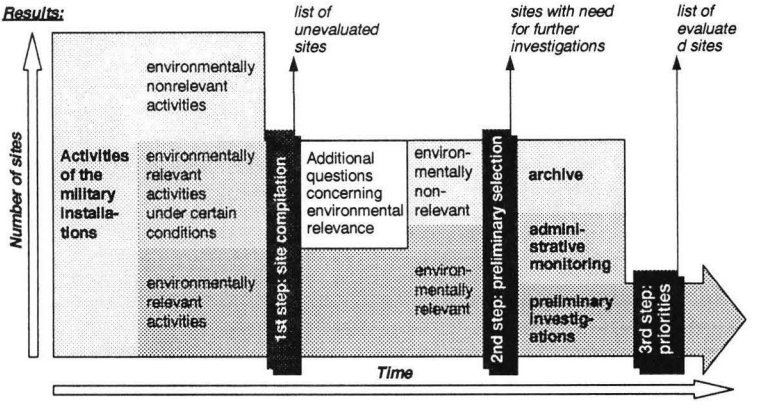


Fig. 3: Procedure for compiling data, in 3 steps

4.2. Strategy, procedure

The project management has set the aim of compiling the register of all DDPS land plots and evaluating them according to the procedure defined by the Swiss EPA over a two year period. Switzerland has been divided into 4 working regions for this project. In each region an engineering firm has been commissioned to compile the data necessary for the register, in close collaboration with those responsible for DDPS installations.

This data compilation is carried out in 3 steps through which the number of the sites to be evaluated is dramatically reduced. Thus the human and financial resources of the project may be targeted to the problem sites early on.

It has been shown that military personnel in the installations who are responsible for environmental questions must be thoroughly introduced to the concept of contaminated sites early on in the project, and must be closely monitored during the compilation of data. In particular, there was some misunderstanding of the difference between the treatment of contaminated sites resulting from past activities and accident prevention during current activities. The data compilation from the DDPS installations is generally comprehensive and has been carried out thoroughly.

4.3. Results, future proceedings

It has been shown that throughout Switzerland approximately 2'500 of 7'500 sites with environmentally relevant activities need further investigation. Only after historical investigation of the activities, and the taking and testing of samples, can it be determined whether a site should be designated as contaminated and thus undergo remediation. The priority list on the register of potentially contaminated sites shows which investigations should be undertaken first, and where the available financial resources for the investigations and remediation may be implemented mostly efficiently.

The database of the register is linked to the real estate information system of the DDPS, so that the need for action during construction or liquidation may be recognised in a timely manner. The information contained in the register will also be made available to cantonal environmental authorities.

5. APPROACH, METHODS AND REMEDIAL ACTION CRITERIA FOR ASSESSING CONTAMINATED SITES (C. Munz)

The approach developed for the assessment of contaminated sites in Switzerland is based on the following goals, facts and thoughts:

1. The main goal is to stop sources of pollution that lead to, or have the potential to result in, hazardous and therefore unacceptable immssions in a legally protected medium, such as groundwater, surface water, soil, air, humans, etc.
2. Zero emissions from contaminated sites are, with few exceptions, not necessary from the point of view of the whole environmental. In addition, zero emissions are often neither technically nor financially feasible. Remedial measures implemented must, however, assure a long-term and sustainable reduction of hazards.

For the quantification of the site hazard (potential) a set of intervention values for an aqueous phase (mg/L) and a set of intervention values for a gaseous phase (ppm) have been defined. The intervention values proposed are compound-specific, e.g. 17 inorganic and 54 organic compounds, plus total petroleum hydrocarbons (TPH) for the aqueous phase. The numerical values correspond to the existing maximum contaminant levels (MCL) for drinking water, where available. Otherwise, the values have been toxicologically derived from the unit risk approach according to the U.S. EPA. The underlying assumption is that a leachate or pore water infiltrating into groundwater should not exceed drinking water limit values for any individual compound.

A "suspected contaminated site" filed in the register will probably - depending on the authorities' estimated site hazard ranking - have to be characterized by a historical and technical investigation. The interpretation of this initial field investigation and the resulting site classification through application of the aqueous phase intervention values,

as well as that resulting from direct groundwater measurements, is schematically shown in Fig. 4. Fhe following four possible site classification options will result:

a) Non-polluted site (no contamination above background identified)
b) Polluted site (some contamination above background present, but *no action required* as no immissions identified and/or no intervention value is exceeded)
c) Polluted site requiring *monitoring*
d) Polluted site requiring *remedial action* = "contaminated site"

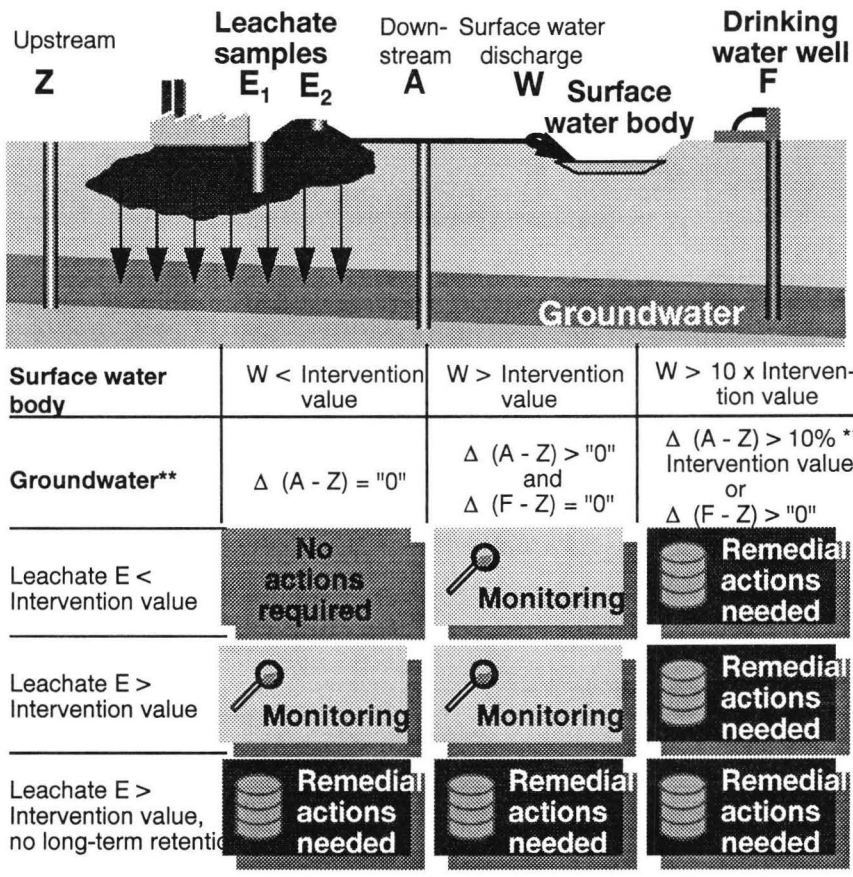


Fig. 4: Scheme of the assessment criteria for the determination of remedial action needs resulting from effects on water bodies (** criteria may vary depending on significance of aquifer; numerical value(s) still subject to discussion).

It must be noted that if contamination attributable to a given site is identified in a well for drinking water, that site will always be classified as a "contaminated site". By considering the difference between downstream and upstream groundwater quality, it is ensured that only the site specific emissions and immissions are taken into account. By comparing the bottom two rows in the figure, it can be appreciated that also the presence or absence of natural (e.g. low permeability subsurface layers) or engineered (e.g. asphalted surface) barriers that significantly reduce the potential rate of emissions from a site are accounted for in the overall evaluation scheme.

For the evaluation of solid samples a leaching test with a continuous upflow column is required. This test is quite similar to column leaching tests, used in Germany, France and the Netherlands. A simple one-page spread-sheet model is being developed, which is based on phase equilibrium partitioning and will provide order-of-magnitude estimates of leachates, soil-gas, and/or expected groundwater concentrations, and can therefore be used as an intial or complementary screening tool.

If a site is classified as a "contaminated site" based on the initial field investigation the further actions required are a detailed site investigation, risk assessment and possibly a feasibility study of remedial options. Based on these investigations the urgency and extent of remedial measures will be defined. The goal of remedial measure(s) is simply defined as the correction of the situation that led to the classification of the site as a "contaminated site". All types of remedial measures -- decontamination, containment, monitoring (e.g. intrinsic bioremediation) and restricted site use -- are acceptable, provided that a long-term and sustainable solution will be achieved.

The approach outlined above will provide a uniform technical and legal framework for the assessment and remediation of contaminated sites in Switzerland. At the same time it does, however, also ensure the flexibility needed to design optimal, case-specific remedial schemes: as much remediation as needed, not as much remediation as possible.

6. OWNERS - PURCHASERS - FINANCIAL INSTITUTIONS - AUTHORITIES: CONFLICTS AND SOLUTIONS (A. Kyas, M. Jaggy)

For some years the consideration of environmental issues has been part of credit approval procedures, not only in UBS but also in three other major banks in Switzerland. The creation of registers by the Swiss authorities of suspected contaminated sites started approximately 10 years ago. Limited attention was paid to these registers until lenders started to use them as an instrument for the identification of financial risks associated with contaminated sites.

Conflicts	Solutions
Statement 1: Owners have been surprised and upset when informed by the lenders and not by the authorities that their property has been registered as suspected site.	• The authorities to inform owners if a property is registered as suspected site. • Open access to information for site owners
Statement 2: Due to the costs of further investigation and possible remediation measures which may subsequently arise, the value of a property is already reduced by the fact of its registration.	• Proactive, environmental site management (active and not reactive). • Attack problems of site contamination in good time: Explore and investigate the site's history, acquire basic information on the company's production and disposal of waste, etc.

Statement 3: Lenders have their own means of identifying the financial risks associated with contaminated sites. Neither the registers nor the environmental risk assessments of the lenders themselves are the cause of the deterioration of assets. Lenders necessarily react to the demands of the stakeholders as well as to environmental legislation and the market.	• Acquire an understanding of the problems of the site; lenders and their corporate banking experts specialising in environment do not need the registers of suspected sites to identify the risks to the environment or public, the credit risks, etc.
Statement 4:Owners or purchasers are not financed if lenders suspect a site contamination. Financial risks can only be identified by an environmental site assessment. Such assessments are the basis for any financial transaction.	• Transparency and cooperation between owners and lenders. • The cost of remediation (financial risks) must be shown in any expert's advisory report. • Advisory reports must be frank and unbiased.
Statement 5: Financial risks are estimated on the basis of the existing environmental legislation, even if local authorities have not been involved in the assessment process..	• More cooperation with the authorities. • The statements of the authorities must be legally binding. • Legal cover is important for all partners involved in the site assessment process.
Statement 6: The site will not be bought if the remediation costs exceed the value of the land. In such cases the development of greenfields will be more attractive to new investment than the reuse of brownfield sites.	Possible measures to avoid the neglect of reusable brownfields are: i) Restrictions on the use of greenfields; ii) Legal decisions must be consistent - a contaminated site may be used after a certain period of time; iii) Financial incentives for remediation, etc.

The recognition and proper management of the risks associated with contaminated sites, together with transparency and cooperation, are the basis for a successful partnership between the lender and the borrower.

NEW DEVELOPMENTS IN CONTAMINATED SITES POLICY IN THE BASQUE COUNTRY

E. Larrañaga (Basque Government Deputy Environment Minister); R. Ortiz[1], J. Epelde[2], J. San Martín[3], I. Muguruza[4], W. Holzwarth[5], G. Zárate[6], R. Sagarduy[7], J.L. Aurrecoechea[8], A. Alvarez[9], J. Galera[10], I. Martín[11], J.C. Blázquez[12], R. San Jorge[13], I. Camiña[14]

Basque Country, Spain : [1]ACLIMA, Parque Tecnológico de Zamudio, Edif. 101, Zamudio-Bizkaia, Spain; [2]BORG SERVICE, Leioa; [3]COINPASA, Getxo; [4]CITMA (GAIKER-LABEIN), Zamudio; [5]GEYSER-HPC, Bilbao; [6]GRUPO HIDRONOR, Algorta; [7]IDOM, Bilbao; [8]IHOBE, Bilbao; [9]IMSITEC, Bilbao; [10]INGURU CONSULTORES, Vitoria; [11]LIMIA Y MARTIN, Getxo; [12]ONDOAN, Zamudio; [13]RECISUELOS, Bilbao; [14]SADER, Zorroza

Key words: Basque Country, contaminated sites, inventory, priorization, derelict land, landfill, contaminated site investigation, contaminated site remediation

SUMMARY

Although specific new technical, administrative and legal tools had to be developed in the late eighties subsequent to the onset of the first cases of severe pollution in the Basque Country, it is now when these instruments have reached a suitable degree of maturity to start implementing a systematic policy aimed at solving not only everyday soil pollution problems, but also the historical heritage of our industrial past. Moreover, specialised consultants and engineering companies are currently addressing issues related to recovery actions involving contaminated sites.

KURZFASSUNG

Erst am Ende der Achtziger Jahre fing man mit der Entwicklung der technischen Werkzeuge an Verwaltungstechnische und gesetzgeberische Grundlagen wurden geschaffen um konkrete Fälle von Bodenverunreinigungen zu verfolgen.

Heutzutage jedoch ist die Anwendung einer systematischen Politik zur Aufarbeitung unseres industriell historischen Erbes möglich. Gleichzeitig gibt es Gremien und spezielle Ingenieurwissenschaften, die interessante Schritte auf dem Gebiet der Rückgewinnung von verunreinigten Industriezonen machen.

RÉSUMÉ

Même s´il n´a pas fallut attendre la fin des anneés 80 pour l´on commence à développer des outils techniques et administratifs et législatifs spécifiques pour résoudre des cas concrets de pollution des sols, ce n´est que récemment qu´a été rendue possible l´application d´une politique systèmatique qui prétend répondre à l´héritage historique que nous a légué notre passé industriel. Des sociétés de consultants et d´ingeneering, á leur tour, commencent á faire des avancées interessantes dans de le domaine du traitement de sites pollués.

1. FOREWORD

Our disorderly industrial and urban growth has been caused by an awkward orography with very few horizontal spaces available. The driving force behind the contaminated soil policy of the Basque Country is not only linked to a major financial crisis, but also to a crucial urban renovation process. Public institutions, universities, research centres, consultants and private engineering companies have been working on the development and subsequent utilisation of a number of tools needed implement a specific policy ever since the first cases of severe soil contamination were reported in the late eighties.

In the early stages, technical tools were developed within the scope of a series of attempts aimed at solving problems originating from certain types of construction waste that were considered to be an unequivocal sign of pollution. Work is still in progress, however, on some methodological and technical guides that recently fully demonstrated their validity with regard to homogenising and simplifying the difficult task of addressing contaminated soil problems suitably.

It is nowadays, however, when the policy designed to address pollution issues is actually being implemented in a global and comprehensive manner although within the scope of an environmental protection policy. Moreover, all the essential tools needed to face this challenge are already taking shape. The Inventory of Potentially Contaminated Sites, for instance, that covers the totality of Basque municipalities has not only been fully drawn up but has also acquired major relevance as a problem area. Likewise, Parliament debates concerning the draft document of the Contaminated Sites Act will be held in the near future as soon the General Environment Act of the Basque Country is duly approved and subsequently lays down a number of obligations related to the protection and recovery of the environment.

In parallel to the aforementioned institutional actions, whose ultimate purpose is to meet a number of highly pressing social demands, specialised companies, research centres and universities are also working hard to provide a number of technically and financially feasible solutions needed to recover contaminated sites. As an activity, it has been taken on wholeheartedly by the Basque Country.

2. INSTITUTIONAL ACTIONS

Institutional actions and, more particularly, actions carried out by the Department of Land Use, Housing and the Environment of the Basque Government have focused on two general objectives: firstly, disclosing the extent of soil contamination and, secondly, providing management tools which, when applied within the scope of a general soil protection policy, allow for the implementation of far more rational and realistic recovery practices.

2.1. SOIL QUALITY INFORMATION SYSTEM. AN INVENTORY OF POTENTIALLY CONTAMINTED SITES

A large part of institutional efforts have focused on drawing up an Inventory of Potentially Contaminated Sites which currently covers 92 of the Basque Country's most industrialised municipalities where 90% of the population lives. It has also become the core element of another far more ambitious project still in the development stages, i.e., the GEOIKER Soil Quality Geographic Information System. As a system, it does not only provide accurate information on the location and most relevant historical data concerning potentially contaminating activities of the Basque Country, but also supports decision-making as it contains information on the vulnerability of underground and surface waters and whether they are capable or not of affecting human health now or in the future. It has also made it possible to establish a ranking of action plans.

As already mentioned, urban renovation practices in which the Basque Country has become involved have lead to a more sensitive reutilization of sites where contamination has been found. In many instances, "untimely" discoveries of soil pollution have either halted or slowed down major financial projects or even given rise to a range of completely different approaches in view of the impossibility of meeting recovery costs.

Proper management practices of GEOIKER should prevent future repetitions of episodes of this nature. The range implications derived from using the above mentioned data in a number of fields are highly relevant and one of the main points of discussion currently focuses on designing information retrieval processes.

2.2. PRACTICAL MANUAL ON MUNICIPAL ACTIONS INVOLVING CONTAMINATED SOIL MANAGEMENT

Town Halls provide an optimum administrative device for the implementation of an efficient policy against soil contamination. Therefore, and in order to provide incentives for actions at this particular level, a group of experts is currently drafting a "Practical manual on municipal actions concerning contaminated soil management", whose purpose is to provide, firstly, a translation of GEOIKER information system contents into more user-friendly concepts for the local authorities and, secondly, to incorporate variable soil quality to the scope of any procedures carried out under Town Hall responsibility. This manual contains chapters dealing with the incorporation of the "soil quality" factor in intricate and rigid town planning processes as well as procedures supporting decision-making in ordinary and extraordinary interventions concerning concepts such as construction permits or licences to operate, enforcement orders and condemnation orders involving contaminated or potentially contaminated sites.

2.3. THE CONTAMINATED SOIL ACT

Investors, real estate brokers, banks and owners of industrial sites usually come across different types of problems associated to soil quality alterations. They all find it is impossible to dispel their doubts based on the current legal framework.

Any actions carried out in this regard are, therefore, disorderly and usually only take into account the specific wishes of owners, buyers, investors, etc. It is because of this and many other reasons that soil contamination requires a clear-cut legislation capable of structuring actions and clarifying, in particular, any contingencies related to liability issues.

For the first time ever, the General Environment Protection Act of the Basque Country (currently being discussed by Parliament members) has been defined as an environmental resource with full rights. Although the Act, however, does provide the legal foundations needed for soil protection purposes, a large legal gap has been detected in this particular field for which a number of specific actions are required. The following points underline the general philosophy behind the Contaminated Soil Act of the Basque Country:

- Not only is the recovery of contaminated sites addressed, but also the prevention of new pollution episodes as well as a defence against existing contaminating actions.
- Primary areas of attention focus on pollution caused by industrial waste and landfills.
- A clear distinction has been made between pollution produced before and after the Act was enforced. It is considered that subjective liability is the most realistic option for so-called "old" pollution, whereas objective criteria shall be used for "new" pollution episodes.
- The selling of a site or cessation of a possible polluting activity provide the mechanisms needed to implement any actions stipulated by the Act.
- A contaminated site register has been created to issue soil quality certificates based on its information.

3. RESEARCH AND TECHNOLOGICAL DEVELOPMENT ON SOIL CONTAMINATION

Technological Centres as well as the Basque Country University, in conjunction with specialised engineering and consulting companies, play a key role as RTD agents within soil contamination problems in the Basque Country. This role can be splitted into the following groups of activities:

3.1. DEVELOPMENT OF QUALITY AND STANDARD PROCEDURES AND CRITERIA

In order to obtain a sharp information about the actual problem of soil contamination in the Basque Country, it is necessary to standarize procedures, quality criteria, and decision making tools. On this framework, a set of procedures for drilling, sampling, preservation and analysis has been developed and validated. Moreover, RTD agents have collaborated in deriving specific Screening/Guidance Values and in defining a common system for Risk Assessment in the Basque Country.

3.2. CHARACTERIZATION AND ANALYTICAL ACTIVITIES

Technological Centres together with the Basque Country University offers a fully equipped laboratory facilities with a wide range of analytical equipment and expertise able to deal with almost any analytical challenge arising from soil contamination. In fact, every contaminated soil analytical work developed in the Basque Country has been carried out with the help of one or more of these RTD agents.

3.3 ACQUISITION OF KNOWLEDGE ON SOIL REMEDIATION TECHNOLOGIES

Technological Centres and the Basque Country University has been and are nowadays carrying out several RTD projects dealing with different treatment technologies for the restoration of contaminated sites. Biological as well as physico-chemical soil treatment technologies are being tested, evaluated and improved. Also a lot of work has been done on other ways of acquiring knowledge on these technologies, such as literature reviews, attending international conferences, participation in specific networks, contacts with experienced companies and centres throughout the world, etc.

The most important works have been developed on Bioremediation, Solvent Extraction, Soil Washing (particle size fractionation), Soil Venting, Vitrification, Thermal Desorption, SF Extraction, and Containment technologies.

3.4. TREATABILITY STUDIES (SELECTION OF THE BEST AVAILABLE TECHNOLOGY)

Soil remediation technology performance data are not transferable from one site to another. Each site has its own unique characteristics that make direct transfer of technology performance data from other sites risky and thus undesirable. Such characteristics are numerous and sometimes their effect is not so obvious. Hence the need arises for a structured approach to the selection of the most appropriate technology for each individual site. Laboratory treatability studies are a major component of such an approach, especially when dealing with sites contaminated with complex wastes, such as mixtures of organics and heavy metals.

The objectives of a treatability study are to screen various treatment techniques, investigate the physicochemical and/or biological mechanisms responsible for treatment, perform a sensitivity analysis of the technique, assess its feasibility and applicability, and derive design parameters for scale-up. The cost of conducting treatability studies is usually a very small portion of the total cost to clean up a site. However, the information obtained from such studies can result in substantial overall project cost savings and may drastically decrease the likelihood for failure.

The experience gathered by the mentioned RTD agents in the Basque Country in relation to quality criteria, standard procedures, decision making tools, characterization and analysis, and handling of a range of remedial technologies make them an essential partner in any contaminated site clean up action.

4. STRATEGIC ACTIONS

In parallel with these actions it has been necessary to respond by studying and creating specific tools to overcome so-called prioritary problems. In this particular regard, a number of actions have been carried out involving industrial derelict land, industrial waste landfills and sites dedicated to certain industrial activities that are still operational and which, due to their specific features, are associated to a significant soil hazard.

4.1 INDUSTRIAL DERELICT LAND

The so-called "industrial derelict lands" form part of a set of major prioritary goals under the policy for contaminated sites established in the Basque Country. The 1992 inventory identified 474 sites of this nature whose reutilization requires comprehensive treatment for all environmental aspects as well as soil recovery. The following actions have been carried out under this heading:

- Updating work in 1997 of the "Inventory of Industrial Derelict Land in the B.A.C." which does not only register the disappearance of new activities based on the information provided by the 1992 edition, but also provides supplementary data that is highly relevant for the management of sites released for other uses.
- The implementation of a programme covering financial aid whose sole purpose is to adequately manage the demolition and subsequent removal of rubble and/or waste from the site involved.
- The drafting of a manual basically for Public Authorities, demolition contractors and environmental consultants featuring guidelines covering site generation from an environmental standpoint. Said guidelines also cover inventory items, waste management, soil research & recovery as well as building characterisation practices.

Research work into former industrial sites affected by town development plans has continued in conjunction with tool preparation work.

4.2. INDUSTRIAL WASTE LANDFILLS

The Basque Country's Inventory lists 664 landfills, 353 of which only contain industrial waste and 67 have been grouped under the codeposit category (i.e., a mixture of urban and industrial waste). The remaining 244 are landfills containing urban waste, soil and rubble. Many of the landfills that have gradually cropped up after 100 years of intense industrial activity in the Basque Country are currently being encroached upon by expanding urban centres that have been forced to use the scarce horizontal surfaces available together with landfills and uncontrolled waste dumps. In order to avoid a number of major risks derived from this situation, an integral landfill control and recovery plan is being drawn up to optimise resources and also avoid specific isolated actions in which information from the following studies carried out in recent years is being used as a tool:

- An inventory of landfills in the Basque Country (1989, revised in 1991).
- Application of the prioritisation System of potentially contaminated sites to landfills in the Basque Country.
- A study involving landfills located in highly relevant areas whose purpose is to define a series of minimum parameters needed to control the potential problem caused by landfills and to lay down the criteria required to establish priorities adequately (1996).
- A decree for the conditioning and closing-down of landfills containing inert waste (1996).

4.3. INDUSTRIAL ACTIVITIES UNDER OPERATION

The Master Plan for Soil Protection in the Basque Country has specifically focused on a number of activities within the scope of the contaminated soil policy which required special attention due to their potential hazardous effects on human health and/or the environment. In recent years, therefore, special attention has been paid to scrap yards and steelmaking practices involving electric arc furnaces. The aims of these studies were as follows:

- Establishing a theoretical definition for a model related to specific activity characteristics and migration capacity of a number of contaminants in relation to the physical environment.
- Assessing the degree of approximation to said model by studying specific sites.
- Assessing the global relevance of the problem in the Basque Country and suggesting possible corrective actions.

The end results of applying the model to the 222 scrap yards listed in the inventory show that between 40 and 60% of these sites could be causing more or less serious soil contamination due to the presence of mineral oil, 10 to 30% could be polluting surface waters and 8 to 15% could also affect underground water as they are located in areas where aquiferous units vulnerable to pollution have been found.

As regards steelmaking practices involving electric arc furnaces in the Basque Country, it has been reported that this activity has taken place at 29 industrial plants, although thirteen have abandoned this practice. There have not only been harmful effects, however, for the sites where the aforementioned activities have been carried out as the sector has also had a strong effect on a number of landfills basically because of dumping practices involving steel mill powder and alkaline slag. Nowadays, there are thirty-seven landfills where steel mill waste has been detected, seventeen of which are owned by the companies themselves. The latter landfills have become the focal point of attention in this study, whose conclusions are as follows:

- Soil contamination in the vicinity of landfills has been caused by an increase in metal concentration (particularly zinc and lead) produced by the dissemination of steel mill powder in the air.

- Metal concentrations in soil drop as the distance to a landfill increases. The relationship used for this purpose involves the following parameters: natural concentration of metals present in soil, total amount of metal discharged in the form of steel mill powder and distance to a landfill.
- Metal concentrations drop rapidly at increased depths.
- Increased metal concentrations found in soils adjacent to landfills could disallow farming or domestic gardening uses.

5. STUDY AND RECOVERY OF CONTAMINATED SITES

With regard to specific sites that had to be investigated and, in some cases, recovered, the need for actions initially arose from the discovery of hazardous and toxic waste during preparatory work site excavations, something considered to be an unequivocal sign of soil contamination. After these initial cases, mention must be made of a number of reasons that gave rise to studies that eventually lead to the recovery of specific sites:

- reutilization of industrial sites for more sensitive uses;
- closing-down and reutilization of landfills;
- demands made by potential buyers, investors and banks regarding soil property conveyances;
- demands made by local authorities (applications for construction permits, changes in the location of potentially contaminating activities, suspected ill effects for human health or ecosystems, etc.)
- studies on the level of environmental impact caused by road construction work.

As far the Basque Country is concerned, a number of companies specialised in environmental matters have decided to set up specific departments to meet research requirements. In recent years, part of their work has also focused on recovering contaminated sites.

5.1. STUDIES INVOLVING CONTAMINATED SITES

Although there is no specific legislation with regard to contaminated soil, the aforementioned reasons have served as an encouragement for certain Basque companies to evaluate approximately eighty sites in recent years according to the procedures defined for such purposes.

A large number of industrial sites and landfills as well as certain sites owned by companies currently in business have been characterised, although a highly relevant role has been played by a study addressing more than 35 sites where uncontrolled discharges of lindane (HCH) pesticide production waste have been detected and have basically been scattered throughout the province of Bizkaia. The final outcome of this study has been used to design action strategies capable of reaching a global solution.

Likewise, mention must be made of the characterisation of 4 sites (approx. 100 Ha in surface area) owned by a leading steel manufacturing corporation which are situated in three privileged areas -as far as reutilization is concerned- and which will eventually give rise to the drafting of recovery projects scheduled for 1998.

5.2. RECOVERY OF CONTAMINATED SITES

As an activity, the recovery of contaminated sites is still in its early stages in the Basque Country. A number of experiences, however, have already taken place in this field; some of them focused on checking whether certain recovery technologies could be applied, whereas others concentrated on upgrading volumes of soil found to be in an unacceptable condition.

In view of the many urgent actions carried out to date, there is no doubt whatsoever that confinement of contaminated soil in safety cells has been the option chosen in a majority of instances, even if temporarily.

Moreover, and with regard to sites contaminated by HCH, a safety cell has been constructed and another project is already in progress involving construction work for another cell designed to store contaminated soil from excavations at 20 uncontrolled landfills. In another nine cases it has been necessary, due to a number of reasons, to take on customised solutions for on-site soil confinement. It has been technically or financially impossible to carry out any actions at seven landfills. Therefore, it has been necessary to implement a control and monitoring strategy whose results shall be used to decide if corrective actions are required.

Other specific actions have also led to the excavation and confinement of dug-up materials in custom-made cells or suitable landfills for each type of waste. This approach, however, is considered to be a temporary, although necessary, solution to prevent soil contamination from seriously hindering urban and industrial development projects.

Special mention must also be made of the recovery of 315,000 metric tons of soil, excavation and demolition rubble contaminated by aromatic polycyclic hydrocarbons and heavy metals (arsenic, lead, cadmium, chromium, copper, nickel, mercury and zinc) originating from a site where steelmaking activities have taken place for decades. Actions were carried out in two stages: in stage one, and after analysing a number of technological alternatives available in the market, all materials were screened to separate any contaminated fragments to be sent to a sinter plant; in stage two, all excavated or demolished materials were assessed to establish whether they could be reutilised for cement manufacturing purposes.

Although contaminated soil recovery has not yet become a far-reaching activity in the Basque Country, local consultants and engineering companies are currently making major efforts to implement technical solutions for our community's specific pollution problems.

A soil granulometric grading plant is currently being implemented for the ultimate purpose of demonstrating how feasible classification methods are when applied to high clay soils, as is the case of the Basque Country (average clay contents 30%).

Laboratory or pilot technologies have also been tested in parallel as a possible solution for any problems areas that cannot be solved by know-how currently available in the market. Likewise, specific cases of soil contamination have made it necessary to apply the following recovery techniques, among others: Pumping and treatment of underground water; Gas drilling and processing; Construction of hydraulic barriers.

FINLANDS COUNTRY SESSION

A. Seppänen[1],J. Puolanne[2], M. Kukkamäki[2], P. Huttula[3], K. Kalevi [2], J. Puhakka[4], J. Tuomainen[2] and O. Pyy[2],

[1] Ministry of The Environment, P.O.BOX 399, 00121 Helsinki, Finland
[2] Finnish Environment Institute, P.O.BOX 140, 00251 Helsinki, Finland
[3] Finnish Petroleum Federation, P.O.BOX 188, 00131 Helsinki, Finland
[4] Tampere University of Technology,P.O.BOX 541, 33101 Tampere, Finland

Key words: contaminated sites, policies, national laws, costs, inventory, national programmes, clean-up technologies, groundwater treatment, PCDD/Fs

SUMMARY

In Finland problems related to contaminated soils have been studied systematically in the 1990s. Some 10 000 sites suspected to be contaminated have been plotted and their actual environmental and health impacts are being investigated. Legislation and remediation metods suited to cold whether conditions have been developed and public funding has been directed to investigation and remediation of sites whose ownership is unclear. Attention has been focused on solving problems related to sawmills and impregnation plants and remediations of oil-polluted sites. More than 500 urgent sites have been cleand up. An important part of the work has been financed with private funds.

KURZFASSUNG

In Finnland wurden die durch kontaminierte Standorte hervorgerufenen Probleme in den 90er Jahren systematisch erkundet. Rund 10 000 möglicherweise kontaminierte Standorte wurden erfasst und mit der Untersuchung der vorliegenden Umwelt- und gesundheitlichen Einflüsse begonnen. Die Gesetzgebung und speziell für das kühle finnische Klima geeignete Sanierungsverfahren wurden entwickelt. Die Untersuchung und Sanierung aufgegebener Industriestandorte wurde mit öffentlichen Mitteln unterstützt. Besondere Aufmerksamkeit wurde den durch Sägewerke und Druckimprägnierungsanstalten verursachten Problemen und der Sanierung von durch Ölprodukte kontaminierten Standorten gewidmet. Mehr als 500 als vorrangig eingestufte Standorte wurden saniert. Die Maßnahmen wurden zum größten Teil mit privaten Mitteln ausgeführt

RÉSUMÉ

En Finland le prombléme creé par les terres polluées a été resolu d'une manière systémathique. Quelques 10 000 emplacements suspects d'être pollués ont été localisés et des études concernant leurs effets sur l'environnement et sur la santé ont été commencées. On a developpé la legislation ainsi que les methodes de purification et de restauration en particulier aptes au climat froid. En plus, des fonds publiques ont été accordés à la recherche età la restauration des terrains sans propriétaire. On a attaché une importance particulière aux problèmes causés par les scieries, les installations d'imprégnation du bois, et les terres polluées par le pétrole. Plus de 500 emplacement urgents ont été restaurés, la pluspart financés par des ressources privées.

1. SOIL CLEANUP POLICY, LEGISLATION AND ADMINISTRATION

In the Report to Parliament on Environmental Protection given by the Council of State in 31. may 1988 is the following statement handling policy on contaminated sites in Finland:"Studies will be made of contaminated land areas, and steps will be taken as necessary to clean them up systematically. The most urgent reclamation work will be investigated as soon as the need for it is established. The following measures will be necessary to achieve this objective: appropriate administrative arrangements must made in the environmental authorities; techniques must be investigated and organized; and, where necessary, work must begin on revisions in legislation. As far as possible, the Polluter Pays Principle will be held to in meeting costs."

1.1 Legal backgroud

Finnish legislation of primary importance in connection with soil contamination are firstly waste management legislation and secondly public health legislation and water legislation. There is no speparate legislation concerning soil protection or remediation of contaminated soil. Contaminated soil have been defined as waste.

The Waste Management Act, the main remedial tool for soil cleaning in older sites (born up to 1.1.1994), puts the responsibility firstly to the polluter or to the owner or occupier of the property or the real estate. In such cases, where it is impossible to find a property owner or occupier the municipality has the secondly responsibility of risk assessment and remediation.

Soil concervation has been included in the new waste legislation (The Waste Act, in force since 1.1.1994) as a separate chapter. In the Waste Act, new soil polluting activities will be prohibited or the soil must returned to its original state so that it can be used to any purpose to which it could have been used without the contamination. The Waste Act will also give the owner of property a responsibility to find out the state and contamination of the property and to transfer this information to the buyer. The Act will also enable the State Council to give detailed regulations concerning soil contamination.

There is also other legislation as those for public health, air pollution, construction and neighbour relations including certain licensing procedures. Water legislation prohibits pollution of ground and surface waters. However, the latter may be polluted based on a license issued by the Water Court or, in minor water affairs, the municipal Board for Environmental Protection.

The links between soil contamination data and land use planning must be improved. This can be done in the framework of building legislation. Land areas prejudicial to health if used may not be built on, nor may they be made subject to planning if such a risk would ensue where the plans to be implemented. The existence of contaminated soil must therefore be known whenever land use is planned. If contamination is suspected, the lacking information must be acquired before decisions are made.

The legislation of compensating environmental damages must also be taken to consideration. The Environmental Damage Act which came into effect 1 st of June 1996 is applied to new

environmental damages. To those damages which occure outside the scope of this Act other regulations such as Damage Compensation Act and the Adjoining Properties Act are applied. In some cases the liability is based on the principles developed in the legal practise. In regard to the damages which took place prior the Environmental Damage Act the laws which were in effect at the time of the damaging event are applied. The applicable law defines the severity of liability and the conditions for sufficient proof. In this respect the Environmental Damage Act applies strict liability entrepreneurs.

On the base of the total evaluation of environmental damage legislation, the injured party is not protected in all cases of damage, although the area of judicial liability has expanded. There is no compensation for damages if the damaging party is unknown or insolvent. Therefore a complementary scheme was up to improve the situation of the injured party.

Expanded liability for damages means that in many cases it is easier for the environmental authorities to recover damage preventing or clean up costs from the damaging party, than earlier.

1.2 Administrative structure

The Ministry of the Environment is the national environmental authority. It formulates environmental policies and does strategic planning. It is also responsible for preparing legislations, setting binding standards and allocation of public funding.

The regional environmental administration is proved by 13 Regional Environmental centers. They are responsible for data collection and allocation of public funding. They creat and run clean-up programmes, give permits for clean-up works and plan state waste managementworks. The Muncipal Boards for Environmental Protection supervise local environmental affairs.

The Finnish Environment Institute conducts environmental R&D. It provides independent expertise for the identification, assesment, clean-up and control of chemically contaminated environments including contaminated soil.

1.3 Financial aspects

At the moment urgent remedial works will be carried out without waiting for the priority plans of contaminated soil remediation. If the polluter still is there or exists, he has the economical responsibility and the polluter-pays principle should be applied. This is not possible if the polluter is no longer there or does not exist any more.

In this case the owner of the real estate has the environmental responsibility. If the owner of property is not able to pay, the municipality has the economical responsibility to remediation and if the costs are high compared to the costs of waste management in county, state can take part of remedial works. There is a current state waste management system which makes it possible for the state to participate or finance (on average by 60 %) remedial action in co-operation with the municipalities. So far the system has been applied about in 90 cases.

However, the system suffers from both a shortage of appropriate funds, whether from local authorities or the government, and its very strict terms of application.

It seem obvious that remediation costs of old contaminated soil sites will often fall upon municipalities and the state if the property owner or occupier or the polluter cannot carry out the work. The situation has been foreseen and about 35 million of FIM have been allocated into this purpose in the state budget each year.

In 1990s there was proposals of committees and working groups of secondary compensation for environmental damage including old contaminated sites. It was proposed that the complementary scheme like separate fund, would be funded by charges levied on dangerous chemicals and waste and by budgeted financing. However, as a result of these proposals was new law in 1998, but in its sope are only new damages. The complementary scheme for compensating new environmental damages including contaminated sites is funded by charges levied on firms (about 3000) using dangerous chemical etc. Restoration of old abandoned sites is funded by budgeted financing.

2. A NATIONAL CONTAMINATED SOIL SITE SURVEY AS A BACKGROUND FOR A NATIONAL CLEAN-UP APPROACH

Only in the early 1980s was soil contamination understood to constitute a more general problem in Finland. Until then it had been dealt with on a case by case basis. Many serious cases were caused by introduction of contaminants via soil into groundwater. At most sites measures were taken and the source was put under control, but at many sites the final clean-up has not yet been carried out.

The first attempts to evaluate problems related to soil contamination were initiated in 1985 with studies and research into the environmental impacts of hazardous waste in landfills. A few years later, a pilot study on contaminated soil sites was carried out. In 1988, the Government promised to asses and solve the problems of soil contamination systematically. At the end of 1989 a special nation wide project by the environmental authorities, later called as the "SAMASE" project, was set up as a substantial part of the effort to keep that promise. The project was a common effort of all levels of environmental administration.

The project was mainly financed from government grants. However, a considerable part of the work was carried out by civil servants. The total amount of work was estimated to more than 60 manyears. During the project, 16 sites were remediated or prepared for remediation.

2.1 Definition of soil pollution

In the beginning of the project, soil contamination was defined as an excess content of harmful substances in the soil, causing significant acute or long-term hazards to human health or the environment. However, radioactive pollution was excluded since radiation was regulated by special legislation and authorities. Also polluted sediments of watercourses were excluded except when the pollution extended to the neighbouring land.

The SAMASE-project set preliminary soil contamination values (guideline and limit values) to be used during the project and thereafter. These were derived as a summary of the most recent information abroad and comparison of existing domestic data eg. on soil quality. According to the proposal, soil with concentrations of noxious substances below the guideline values could be used without restriction for any purpose whatsoever. Limit values could be applied to soil that can be used with reservations when the need for cleanness is not so great. Deviations from these values could be accepted in individual cases on the basis of a risk assessment.

2.2 Site identification and investigations

A list of potentially contaminated sites was collected in the regional environment administration. An extensive amount of information sources such as permits, protocols, announcements, chemical and oil combatting incident reports and other documents on polluting activities or events was screened. This information was collected from waste management, water, public health, construction and regional planning authorities. Also other than official sources such as old catalogues of industrial associations, registers, maps etc. were used. Altogether more than 20 different sources of information were utilized.

All acquired information on potentially contaminated sites was entered in a register. Lots of sites were visited and those considered as most harmful were investigated preliminarily. Risks to the environment were assessed mainly based on existing information using a preliminary risk classification. Due to the relatively strong water-related expertise in the administration, risks to ground water aquifers were perhaps evaluated better than other risks. As the quantity and quality of existing information on the pollution was very restricted, detailed risk assessments and priority rankings were impossible.

2.3 The extent of soil pollution

The total number of suspected contaminated sites was 10 400. Had all minor sites been included, the register might have contained up to 25 000 sites. The soil was designated as clearly contaminated at 650 sites; 90% of all sites were designated as probably or possibly contaminated. More than 2 000 of the sites were in ground water areas and 1 600 were close to residential areas (table 1). Further studies and analyses were considered necessary for at least 2 000 sites.

Table 1. Location of suspected contaminated soil sites by risk classes (SAMASE-register).

Location	Risk class*)				
	01	02	03	04	Total
GW-area**)	27	940	381	102	1 450
< 100 m from R-area***)	28	610	338	113	1 089
GW-area and close to R-area	17	375	168	36	596
Other area	177	5 430	1 252	402	7 261
Total	249	7 355	2 139	653	10 396

*) 01 contamination insignificant
02 minor contamination possible, spreading not probable
03 contamination and spreading suspected
04 contamination and spreading verified by investigations

**) Ground water area

***) Residential area

Most cases of soil contamination were caused by garages, scrap yards, waste treatment plants (including landfills), sawmills and wood impregnation plants (table 2). The total volume of probable clean-up work was assessed mathematically. The number of polluted land areas expected to require restoration over the next 20 years was put at around 1200, of which 800 are contaminated industrial and other such areas (5,4 bill. FIM = 1,2 bill. USD), over 300 old landfills (1,1 bill FIM) and 35 mine tailings areas (1,4 bill FIM)(table 3).

Table 2. The number of suspected contaminated sites by polluting activity (SAMASE-register).

Polluting activity	Number	Percentage of all (%)
Scrap yards and repair shops	1 701	16
Waste treatment sites	1 682	16
Sawmills and wood impregn.	1 032	10
Service stations	816	8
Metal industry	607	6
Wastewater treatment plant	560	5
Concrete industry	526	5
Others	3 472	33
Total	10 396	100

Table 3. An estimate of the number of sites to be cleaned and respective costs of soil clean-up during the following 20 years.

Site type	Number	Costs 10^3 million FIM	Old sites*)
Industrial sites	808	2,96	27 %
Landfill sites	334	1,08	57 %
Mine tailings	35	1,40	54 %
Total 1 177	5,44		

*) Contaminating activity has ceased in 36 % of all suspected sites in the register. The total clean-up costs of these sites is 2 200 million FIM.

2.4 Other problems encountered

Soil contamination causes several challenges to financing, legislation, site assessment, land use planning etc. which were addressed in the project. New waste legislation was drafted simultaneously and the findings of the project could be directly applied.

By and large, the findings and proposals of the project have constituted a firm base for future measures and programming of clean-up, including a surprisingly good response by the whole environment administration and decision makers.

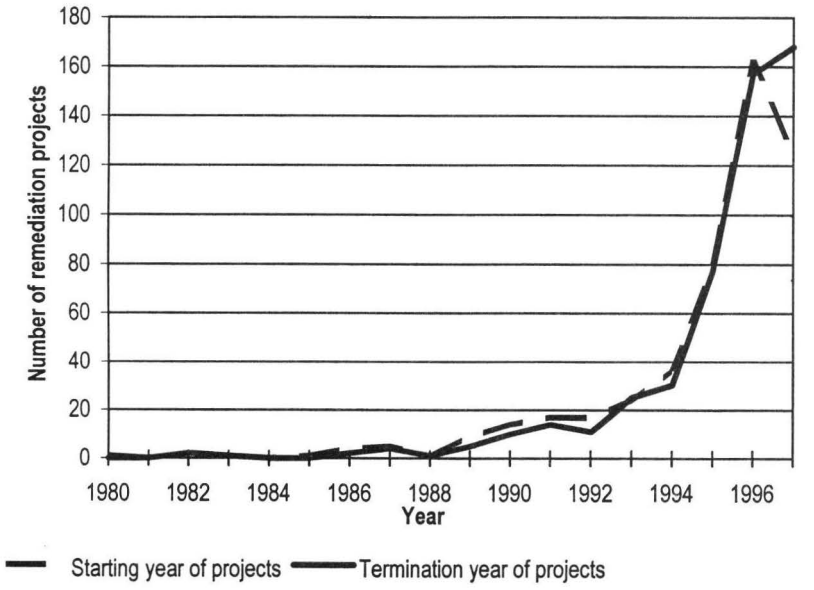
Puolanne, J. Pyy, O. and Jeltsch, U. (1994) *Contaminated soil sites and their management in Finland. Memorandum 5/1994, Ministry of the Environment, Department for environment protection. Helsinki, Finland (in Finnish with English summary).*

3. PRESENT CLEAN-UP ACTIVITIES AND RELATED R&D

3.1 Information about recent clean-up operati

Systematic restoration of contaminated sites began in the mid 1980s. Until then contaminated sites had been cleaned up mostly in connection with pollution incidents, as part of the combatting operation. After the report of the above-mentioned survey was published there was increased awareness of the problem, followed by a clear rise in the number of identified remediation sites. At the same time more and more state funds were allocated to remediation works. One of the reasons for the increased allocations was that the government tried to bring down the rising unemployment figures by creating jobs in the environmental sector.

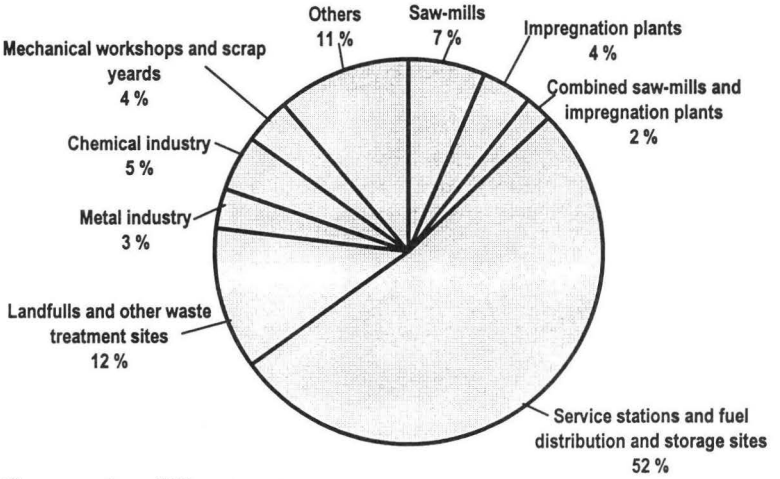
Lately the number of clean-up sites has risen to about 150 sites a year. When the national clean-up programme for decommissioned service station locations will start, the number will temporarily rise to 200 - 250 sites a year. All in all some 500 sites have been cleaned up during the last 15 years, most of them after 1995 (Fig. 1). If the so-called post-combatting measures were taken into account the figure would be considerably higher. Post-combatting measures, i.e. the clean-up works done immediately after an accident, were not properly registered earlier and their exact number is only known from the last few years. The improved situation is also a result of more stringent supervision and a comprehensive licencing system for the clean-up of contaminated soils.



Figur 1. Number of remediation projects starter and terminated.

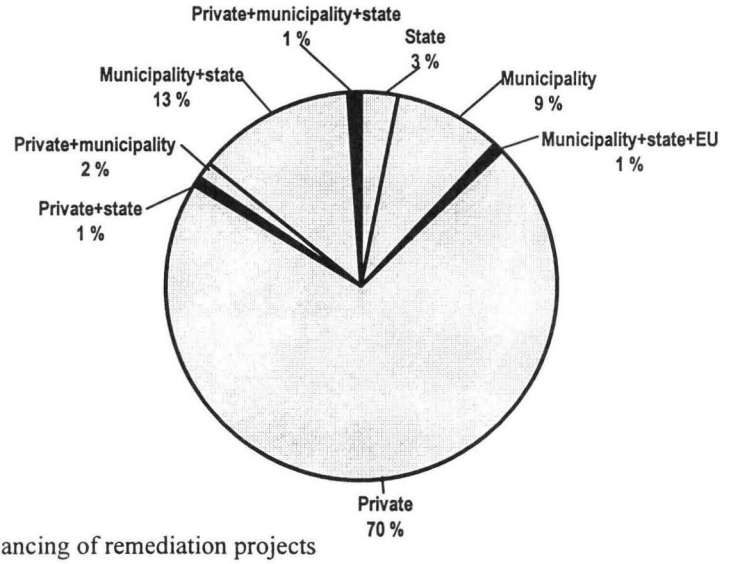
More than 50% of the clean-up sites are sites that serve the distribution, transportation and storage of various kinds of fuels. Another category of important sites are landfills and other

waste treatment areas (12 %) and former locations of saw-mill industry or wood impregnation operations (13 % in total) (Fig.2).



Figur 2. Clean-up sites different sectors.

The costs per site have varied greatly. The remediation of sites contaminated by fuel has cost on an average 300 000 - 500 000 FIM per site (50 000 - 90 000 ECU per site), while other sites have been two to three times more expensive. About 70 % of the number of sites have been financed privately and the rest jointly by the state, municipalities and the private sector. When the governmental environmental authorities have been responsible for the clean-up, the state share of the total expenses has normally been 50 %. In those cases where the state has not been responsible for the implementation of the clean-up project, the state share of the costs has been 30 % at the most (Fig. 3).



Figer 3. Financing of remediation projects

Annually government funds used for the clean-up of contaminated soils has been at a level of 35 million FIM (6 million ECU). With these funds the state has been able, through the rules that govern state participation, to control the use of some 80 million FIM (14 million ECU) for the remediation of contaminated soils. In total about 200 million Finnish marks (34 million ECU) are used in Finland annually for the restoration of contaminated soils. An important part of the private funds is used in the biggest cities Helsinki, Turku and Tampere for the clean-up of old industrial sites for housing purposes.

3.2 Remediation methods

Common remediation methods used in Finland are
- composting of soils contaminated with organic substances, either in-situ or at separate treatment sites,
- stabilisation of soils contaminated with inorganic substances and their final disposal at the remediation site or use in liner systems at landfill sites,
- purification of the pore air of soils,
- containment,
- incineration in high or low temperature, and
- disposal of slightly contaminated soils at landfills.

Washing techniques and biological in-situ methods have not been applied in full scale.

3.3 Problems encountered

In principle and in the legislation the liability for remediation has been defined very clearly: the polluter pays. In practice, however, the liable party is often resourceless, bankrupt or out of reach for the authorities. In some cases the contamination has not been caused intentionally and the requirement to restore the site would be unreasonably severe. But even when the public sector participates in the remediation, the future liabilities and duties must be clarified. It is also important to solve how to take into account the added value of the restored site.

It is not always self-evident what is the correct remediation method and how to implement the project in an optimal way. Highly qualified consultants for remediation projects are not very numerous, and the qualitiy assurance may not always work. The situation is, however, rapidly improving as the activities are gaining more ground and the requirement levels in the different parts of the country are being harmonized, and more know-how is available.

In some cases there have been problems with reutilization and final disposal of decontaminated or treated soils. There has been a shortage of reception sites and treatment sites. However, the problem is being solved through free competition, kept under control by the licencing system. Development has been slowed down by the uncertainty among the entrepreneurs about the scale of the activities and to what extent it is profitable to invest in the infrastructure required by soil clean-up projects.

3.4 Research and development

Research and development work is being carried out in the following fields:

Sites contaminated by organic substances
- composting of soil contaminated by oil and chlorinated phenols
- purification of soil contaminated by dioxins and furanes (containment, incineration, biological decomposition ?)
- use of fungi for aerobic decomposition
- use of plants (vegetation) in the clean-up of oil-polluted soil
- biological filters for the gases from pore air purification

Sites contaminated by inorganic substances
- consolidation and stabilization techniques and additives used
- use of plants (vegetation) in the purification of soil contaminated by metals
- movement of compounds in soil and their fixation

Clean-up and restoration methods
- biological in-situ treatment of soil and groundwater
- liner systems and materials used at landfills; frost problems

Other development work
- criteria for the utilization and disposal of treated soil
- risk assessment and environmental impacts of contaminants
- legal and economic liabilities in decision making and in accounting
- model projects (restoration of shooting ranges, disposal sites for mine tailings)
- standardization of soil analyses (Nordtest cooperation)
- improvement of reliability and rapidity of field analysers and biological test kits
- quality assurance and documentation in soil restoration works.

Many state research institutes and universities and other academic institutions carry out research and development related to remediation of contaminated soils. Also private manufacturers of equipment, consulting companies and contractors involved in soil remediation are developing their own commercial applications. A common feature in most of these projects is that they deal with methods suited for cold climat.

4. THE PETROLEUM INDUSTRY'S PROGRAMME TO REMEDIATE POLLUTED DECOMMISIONED SERVICE STATION SITES - SOILI

The Finnish Petroleum Federation (FPF) is implementing a programme for the remediation of sites which have been used for retail sale of petroleum products. The programme will remediate soil that was polluted by oil from the service station or other outlet activities that took place on these sites.

The programme is based on an agreement between the Finnish Petroleum Federation, the Ministry of the Environment, and The Association of Finnish Local Authorities, done in Helsinki Nov 19, 1996. It is being funded by oil industry marketing companies, Oy Esso Ab, Neste Marketing Ltd., (Neste and Kesoil chains), Oy Shell Ab, as well as the Oil Pollution Compensation Fund, operating in connection with the Ministry of the Environment, to which oil companies pay a fee levied according to their oil imports to Finland. The programme's practical implementation is the responsibility of the Oil Industry Service Center Ltd (OISC), a company owned by the FPF.

The nation-wide ten-year programme offers holders of former service station sites an opportunity to solve an otherwise difficult environmental problem. One purpose is to avoid the complex issue of responsibility that often relates to soil contamination that has possibly taken place over a period of decades. Assigning legal responsibility to the parties involved may in many cases prove to be an impossible task. The programme is designed to prevent the creation of judicial problems in advance.

Properties belonging to the following categories may apply for the programme:

- Retail outlets to be closed down or already closed, but possessed by oil company or retailer belonging to the distribution chains of the participating companies (collective financing by oil companies).
- Equivalent retail outlets closed earlier, for which it is not possible to identify the party responsible for the damage or the party otherwise responsible for remediation ("hostless sites"), or if such a party is insolvent, or in cases where the accrual of repair costs to the current owner or tenant would be clearly unjustified, (Oil Pollution Compensation Fund).

The most typical distribution locations qualifying for the programme are aged service station or other distribution outlets.

The programme will give property owners the opportunity to remediate their property to its unpolluted condition, enabling it to be considered for other uses. To qualify for the programme, the owner, or owner's designated representative, shall submit an application for soil remediation works to the programme's Management Group. The applications may be submitted by petroleum companies participating in the programme and private or other property owners. In submitting the application, the property owner authorises the OISC Ltd to function on the owner's behalf in establishing the need for soil remediation works, the implementation of these works, and accordingly grants the power of authority to the OISC regarding this aspect of the property.The OISC received 150 applications to the programme before the end of the year 1997.

The collective financing arrangement requires limitations regarding future use of properties cleaned-up. If it is decided to re-establish of retail sale of petroleum fuels on a site remediated with collective oil company financing before a period of 10 years has elapsed from the completion of approved remediation works carried out according to the programme, the owner derived benefit from the programme is obligated to compensate the OISC for all expenses arising from investigations and remediations carried out on the site.

The priority sequency will be set by the programme's Management Group according to the same environmental protection criteria for sites already closed, and well as for those retail sites that are scheduled to be closed and accepted to the programme.First will clean sites that are

the most polluted or where there is a ground water contamination risk (acute environmental or health risk).

5. REMEDIATION OF CONTAMINATED SAWMILL SOIL

Wood preservation with chlorophenols has been done in Finland since the 1930s. At first preservation products were imported from abroad, mostly from USA. Since 1940 a chlorophenol mixture, called Ky 5, was produced in Finland. The total production was about 23 400 tons until its production was forbidden. The production stopped in 1984 and the use was completely banned in Finland in 1988 because of the detrimental effect on the environment and health. The total amount of chlorophenols used as wood preservative in Finland was about 30 000 tons between 1934 and 1988.

Earlier, when the toxic effects of chlorophenols were not recognized, Ky 5 was used very carelessly. Spills and leakages were normal events at sawmills. Also the packages were stored and handled so that leakages to soil were obvious.

The treatment of timber was usually done in two different ways, dipping or spraying. The most common way was dipping. The sawn timber was dipped into a 1 to 2% solution of chlorophenols. Treated timber was dried in the open air or in drying kilns. Dried wood was mostly stored in open air in the storage areas belonging to the sawmills.

During the 1980s the contaminated sites in Finland were registered and remediation of around 50 sawmill sites have been done during the late 1980s and in the 1990s with regard to chlorophenols. Around 500 sites are still to be cleaned up. Many sawmills are located on lake or river shores, due to earlier transportation of wood on the waterways. Typically old sawmills are situated in the centre of smaller towns, and in many cases the areas are attractive for housing.

The new serious problem at the sawmill sites has turned out to be polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F). These compounds have been present as impurities in chlorophenol mixture"formed. At this survey information was inquired on the number of sawmill sites, at how many sites the chlorophenols and PCDD/Fs had been investigated, how many sawmills had been remediated and with which method remediation had been done. Also the concentrations of chlorophenols and polychlorinated dibentso-*p*-dioxins and - furans were inquired.

Altogether 619 sawmills were registered. Chlorophenol concentrations had been investigated in 153 cases and soil remediated in 56. Only at 20 of these remediated sites, the PCDD/F concentrations had been investigated. In almost every case the method of remediation had been composting in biopiles off or on site. To a lesser extent soil had been isolated on landfills or thermically treated. The bioremediation technology had worked out excellently with regard to chlorophenols (Laine and Jørgensen, 1997). After the completion of many remediation events it has become evident that extremely high concentrations of PCDD/Fs can still be found in piles (Laine et al., 1997) and even on sawmill sites. The values recorded exceed the remediation target value (500 ng/kg I-TEQ, international 2,3,7,8-TCDD toxicity equivalent)

with up to 26 times and the limit value for non-contaminated soil (20 ng/kg I-TEQ) with up to 370 times (Kalevi et al., 1998).

In the future it is important to measure the concentrations of PCDD/Fs during the first investigation of a sawmill site, where chlorophenols have been used. This allows to perform a proper risk evaluation and provides the data to plan the sufficient remediation.

Kalevi, K., A. Donner, H. Kiviranta, T. Vartiainen, K.S. Jørgensen. 1998. Occurrence of polychlorinated dibenzo-*p*-dioxins and dibenzofurans as impurities in wood preservative contaminated and remediated soil. *These proceedings (ConSoil'98).*

Laine, M.M., J. Ahtiainen, N. Wågman, L.Öberg, and K.S. Jørgensen.1997. Fate and toxicity of chlorophenols, polychlorinated dibenzo-p-dioxins and dibenzofurans during composting of contaminated sawmill soil. Environ. *Sci. Technol. 31:3244-3250.*

Laine, M.M. and K.S. Jørgensen. 1997. Effective and safe composting of chlorophenol-contaminf BF&V.

6. KÄRKÖLÄ SAWMILL GROUNDWATER PUMP AND TREAT EXPERIENCES

In the municipality of Kärkölä, Southern Finland, serious groundwater contamination was observed in 1987. The chlorophenol contamination was traced to an adjacent sawmill which had, for decades, used a wood preservative consisting of mainly of 2,3,4,6-tetrachlorophenol (TeCP),2,4,6-trichlorophenol (TCP), and pentachlorophenol (PCP). Chlorophenols had apparently been released to the soil during normal operation. Further, a massive fire of the sawmill has been claimed for the reason of a single, large spill. The volume of heavily contaminated groundwater is at least 100 000 m^3 containing over 3 000 kg of chlorophenols. Typical chlorophenol concentrations in the groundwater range from 10 to 40 mg/l. The water intake plant of this aquifer served approximately 3 000 people. Elevated occurrence of non-Hodgkin´s lymphoma in the Kärkölä population may be related to the use of contaminated drinking water or contaminated fish from the nearby lake where the contaminated groundwater is discharged.

Kärkölä case was the first chemically contaminated site in Finland that received wide public attention. It also served as a stimulus for starting contaminated soil reclamation research and development in the country. For the Kärkölä groundwater treatment, several techniques with various degree of success have been and are being tested. These include, for example, activated carbon adsorption, activated sludge, pure culture biofiltration, fluidized-bed biofilms, and *in situ* bioremediation.

At Tampere University of Technology, chlorophenol bioremediation research was started in 1987. This work resulted in a high rate fluidized-bed process which operates at low temperatures (e.g. Mäkinen et al., 1993; Järvinen & Puhakka, 1994; Järvinen et al., 1994; Melin et al., 1998; Puhakka & Melin, 1996, 1998). Our on-going research focuses on *in situ* processes (e.g. Langwaldt et al., 1998; Männistö et al., 1998). The fluidized-bed process has now been used for three years for pump and treat remediation of the Kärkölä groundwater.

The pump and treat process consists of pumping wells, groudwater storage tank, and a 5 m^3 fluidized-bed reactor. The reactor height and diameter are 6.5 m and 1 m, respectively. Sand is used as biomass carrier material. The process is designed to treat 50 m^3 of groundwater per day and operates at 8 °C.

The pump and treat process contains the plume from spreading and has decreased the average chlorophenol concentration in the groundwater from over 20 to below 10 mg/l. So far, approximately 50 000 m^3 of groundwater has been treated with 95 to 99% mineralization of chlorophenols. During steady state operation, the concentration of total chlorophenols in the treatment effluent remains below 50 µg/l. The operation costs are FIM/m^3 groundwater or FIM/g of CP removed.

Järvinen, K.T. and Puhakka, J.A. (1994). Bioremediation of chlorophenol contaminated groundwater. *Environmental Technology*, 15, 823-832.

Järvinen, K.T., Melin, E.S. and Puhakka, J.A. (1994). High-rate bioremediation of chlorophenol contaminated groundwater at low temperatures. *Environmental Science and Technology*, 28, 2387-2392.

Langwaldt, J., Männistö, M.K., Wichmann, R. and Puhakka, J.A. (1998). Simulation of *in situ* subsurface biodegradation on polychlorophenols in air-lift percolators. *Applied Microbiology and Biotechnology*, (tentatively accepted).

Mäkinen, P., Theno, T.J., Ferguson, J.F., Ongerth, J.E., and Puhakka, J.A. (1993). Chlorophenol toxicity removal and monitoring in aerobic treatment: recovery from process upsets. *Environmental Science and Technology*, 27, 1434-1439.

Männistö, M.K., Tiirola, M., Salkinoja-Salonen, M.S., Kulomaa, M. and Puhakka, J.A. Diversity of chlorophenol degrading bacteria isolated from contaminated boreal groundwater. *Applied and Environmental Microbiology* (submitted).

Melin, E.S., Järvinen, K.T. and Puhakka, J.A. (1998). Effects of temperature on chlorophenol biodegradation kinetics in fluidized-bed reactors with different biomass carriers. *Water Research,* 32, 81-90.

Puhakka, J.A. and Melin, E.S. (1996). Bioremediation of chlorinated phenols. In *Bioremediation: Principles and Applications*, Crawford, R.L. and Crawford, D.L. (eds.), Cambridge University Press, Cambridge pp. 255-299.

Puhakka, J.A. and Melin, E.S. (1998). Chlorophenol-contaminated groundwater bioremediation at low temperatures. In *Encyclopedia of Environmental Analysis and Remediation*, John Wiley & Sons, New York (in press).

CONTAMINATED SOIL '98

Technical tour

CONTAMINATION ASSESSMENT TECHNOLOGIES AND REMEDIATION DECISION MAKING AT A FORMER REFINERY SITE

M.D.Lambson[1] and W.J.Syratt[2]

[1] BP International Limited, Sunbury-on-Thames, UK
[2] Environment Matters, Old Windsor, UK, formerly BP International Limited

Key words: Biological treatment; Case study; Groundwater remediation; PAH; Refinery site; Risk management; Solidification / stabilization

SUMMARY
The technologies and decision processes being used to return a former oil shale refinery and surfactant works to beneficial use are described. A tiered risk based process was employed which integrated with the remedial solutions and enabled decision process flexibility and interaction with regulatory authorities. A thorough investigation of the site hydrogeology and the physical and chemical properties of the contaminants identified three material types and associated risks, each with a different remedial solution. Most of the contamination is being dealt with by managing groundwater insitu using cut-off drains with reed bed treatment for dissolved products. Exsitu bioremediation is being used for most of the remaining wastes, while stabilisation is used for unstable tarry wastes. The paper demonstrates how a complex problem can be simplified using hazard & risk assessment to provide a focus, and allow sympathetic and cost optimised remedial solutions.

Contaminated Soil '98, Thomas Telford, London, 1998, 1289–1298

1.0 Introduction

This paper describes the technologies and decision processes which will allow a former oil shale refinery and surfactant works to be returned to beneficial use. The site rehabilitation has three main objectives. These are to clean-up the main site sufficiently to allow return to beneficial use, to deal with tarry wastes from outlying sites and to undertake this work in a manner that protects and/or enhances the environment and the company's reputation.

The initial sections of this paper outline the site history, the origin of the wastes, and the site setting. The decision process and important aspects of the assessment and remediation technologies used during the site restoration are then described. Finally, conclusions are made which demonstrate how a complex problem can be simplified using tiered risk based approaches to allow sympathetic and cost optimised remedial solutions which meet the objective of sustainable development.

1.1 Site History

The Scottish oil shale industry started operations in 1851. It extracted oil through the distillation of coal and oil shale mined locally. The oil shale formations occur extensively throughout the West Lothian region of Scotland. By 1865 there were 120 works producing oil products, particularly paraffin. By the 1920's the oil shale industry had rationalised and on BP acquisition six companies remained.

The Pumpherston Site was used from 1884 until 1962 for oil shale processing and as a refinery site. The original site was larger and included spoil heaps of spent shale (bings) to the east, a brick works to the north and settlement ponds to the south-east (in an area now owned by West Lothian Council). From 1948 the site was also used for the production of detergents. The detergent works closed in 1993 and was demolished. Today only the effluent treatment plant, two warehouses and the office block remain. The present site is owned by Young's Paraffin Light and Mineral Oil Company, a BP subsidiary.

1.2 Wastes

During the refining process the oil bearing shale was retorted by heating up to 1000°C to drive off the organic matter and nitrates. Cadell (1913) summarises the process of manufacture and how the organic matter from the retorted oil shale was used. Only about 20% by weight of the mined shale yielded useful products. Inert spent oil shale was the main waste product (~75%) from the shale oil refining, but refinery tars were also produced (~5%). The detergent manufacturing at Pumpherston involved the sulphonation of feedstock oils to produce anionic surfactants and yielded acid tar wastes. Disposal practices for these were similar to the shale oil tars. At Pumpherston the majority of tar waste is refinery tar. Evidence from site and Ordnance Survey plans suggests that waste disposal ponds were operative at Pumpherston Works by 1895 and they continued to be created and used until about 1957. Figure 1 presents a plan of the works and summarises the location of the tar ponds and other accumulations.

2.0 Site Setting

The Pumpherston site is located on the eastern outskirts of Livingston, West Lothian, Scotland. The site has an area of approximately 28 hectares and lies at an average elevation

of 128m above Ordnance Datum with the natural ground falling from the site to the north, east and south, and rising gently to the west. The main works site (see figure 1) is located to the south of Drumshoreland Road. To the north is a former brick works and part of an old shale bing. To the west lies a golf course and to the south is agricultural land and a bing. The primary surface water receptors are a local stream (Bank Burn) to the south-east, and the River Almond some 1100m distant to the south

2.1 Geology

The general sequence of strata beneath the site comprises:

Made Ground or Fill		0.1 to 5.5m
Glacial Till	(upper weathered)	0.0 to 3.1m
	(lower fresh)	0.0 to 10.8m
Bedrock	(Pumpherston Shales)	22m +

The made ground is variable in composition as well as thickness. It is generally granular in texture being derived from inert spent oil shale (blaes) but with a significant silt & clay content. In some areas it contains much demolition rubble. The glacial till comprises gravelly, silty, sandy clay with boulders. In places the till is absent where ponds have been excavated through it. Beneath the glacial deposits lie the Pumpherston Oil Shales. These comprise a mixed sequence of oil shales, siltstones, sandstones and limestones.

2.2 Hydrogeology

The site occupies a high topographic position, hence the only water flowing off site is derived from rainfall. Annual average rainfall is about 800mm. The cumulative rainfall pattern for Pumpherston displays two main trends, giving 'summer' and 'winter' periods. Winter rainfall rates are typically 3 times higher than summer rates. This has implications for the flushing of contaminants from the ground as a potential migration mechanism. A major factor is the proportion of rainfall infiltration and the capacity of the ground to transmit this.

Groundwater levels at Pumpherston have been measured monthly for some four years by a monitor well network addressing both the upper fill & clay till soils and the underlying rock. Two water tables occur, one perched in the fill & till with the second being deeper and associated with the bedrock. The data reveal a consistent pattern. The highest groundwater levels occur during February with the lowest being recorded during August. For the upper fill & clay till soils the mean annual variation in groundwater level is typically 0.6m (+/- 0.3m). There is a shallow groundwater divide in a NW to SE direction across the site. To the east of this flow is eastwards and then south-eastwards. Here groundwater hydraulic gradients are generally low, being about 0.8% under the former process and 'pond' areas. They increase by about one third close to the site eastern boundary and a railway cutting. To the south of the divide the groundwater flow is generally SSE. The hydraulic gradients are also low, again being about 0.8%. The groundwater flow pattern associated with the rock is adversely affected by under-drainage from the shallow & deep mine systems. This is most prevalent along the site western boundary. However, most of the site the rock is overlain by clayey till soils, an aquitard, and vertical migration is not considered a primary route.

The groundwater monitoring data indicate that lateral migration in the fill material dominates and the groundwater 'driving forces' in this are well understood. Data also confirm two primary migration routes identified by earlier site assessment and the geomorphology. These are SSE across the southern boundary and E to SE along the site eastern boundary towards the Bank Burn. The groundwater table has little seasonal level variation and hydraulic gradients are generally low, being less than 1% over the majority of the site.

3.0 Decision Processes

At first, the Pumpherston site presented a seemingly complex issue, being a large site with a long industrial history and many unknown or ill-defined potential problem areas. Following closure of the detergent plant in mid 1993, a comprehensive assessment of the site was undertaken to ascertain the contamination present and the associated implications for restoration. This was a phased approach as outlined below. Flexible decision and work processes evolved and, together with a tiered risk based assessment framework, these helped focus on the important issues allowing appropriate corrective actions. It integrated with the remedial solutions and planning requirements. The simplification of a complex issue was approached using a six phase process.

- comprehensive desk study using many sources of historical data and aerial photography
- stage 1 site assessment - screening
- initial conceptual model - qualitative hazard & risk assessment, remedial options review
- stage 2 site assessment - focused on remedial solutions, quantified risk work
- monitoring - both on and off site
- refinement of conceptual model and risk assessment

The investigation concluded that there were two classes contaminants at Pumpherston site requiring treatment and/or management - surfactants and hydrocarbons. Much of the hydrocarbon contamination is contained in former waste and effluent 'ponds' which were filled with hydrocarbons and tars and covered up on closure of the refining site.

A Restoration Options Study was then undertaken. This considered the remedial actions most appropriate for the site related to possible end uses for the land. The study examined a range of options from which the most cost effective and environmentally sound scheme was selected. The selected option was further defined by a Front End Engineering Design (FEED) study which recommended the following priorities :

- Secure boundaries - isolation of groundwater using cut-off drains to capture contaminated groundwater. Initially this would be treated in the site effluent treatment plant and discharged to sewer under existing arrangements.
- Treat Groundwater - installation of a reed bed system to provide long term treatment of the contaminated groundwater from the cut-off drains.
- Removal of hardstandings, drains, underground pits and sumps with treatment for any contamination 'hotspots' found during the works
- Corrective action for tar 'ponds' which could pose an unacceptable risk
- Continued monitoring of boreholes and surrounding water courses
- Return site to beneficial use either as an extension to the adjacent golf course or as an industrial development

Hazard ranking and risk assessment were used throughout the investigative and decision making process described above. The level and complexity of these assessments increased as the level of site knowledge increased through the stages of investigation and analytical measurements. Initially, the hazard and risk work was essentially of a qualitative nature. A relative hazard ranking of the tar 'ponds' formed part of the Restoration Options Study. This revealed that in terms of consequence four of the 'ponds' gave rise to some 75% of the likely risk. Further characterisation work on these allowed better definition of the likely risks and refinement of the assessment for the FEED study work. At the FEED study stage several remedial options were examined for the tarry wastes. These included (1) incineration, (2) cement kiln fuel, (3) recycling in current refinery processes, (4) stabilisation, (5) bioremediation, and (6) landfill. Of these, bioremediation and cement grout stabilisation were demonstrated to offer the best combination of effectiveness, environmental benefit and cost. These two options are being progressed within the legislative framework of an existing waste management licence, with agreed amendments. Bioremediation of some of the wastes became a viable option following a tiered health risk assessment which derived site specific acceptable concentrations for key contaminants. This quantitative risk work was undertaken in consultation with SEPA (Scottish Environment Protection Agency). Bioremediation trials demonstrated the viability of the method and full scale treatment operations are now underway. The bioremediated material can be used as topsoil on a golf course development, the likely end use of the site.

One of the most beneficial influences on the investigation, remediation and decision process outlined above was time. Ensuring that sufficient time was available enabled options to be assessed, allowing the implications of each to be fully understood before action was taken. As a consequence of this, overall costs were reduced. Local Planning Authorities and SEPA, or its predecessor bodies, were actively involved in the restoration process from the start. The collaboration with SEPA is described by Pollard & Herbert (1998). By working in partnership with the regulators, the restoration was advanced at a rate consistent with the level of knowledge. This provided high levels of confidence that the overall process would achieve the set objectives. A key element in this process was securing the site boundaries by isolating the groundwater. This enabled the remedial works within the site boundary to be undertaken safely with respect to the wider environment, and within a timescale suited to the methods of treatment. It also enabled material from outlying waste accumulations to be returned to the Pumpherston site for treatment, thereby reducing potential risks. The timescale also allowed the trends from groundwater monitoring to be incorporated into a refinement of the site conceptual model for the final risk assessment work. Again, this provided confidence on the overall understanding of the site, which helped with regulatory approvals.

4.0 Technology Aspects

Many technologies have been and are being used during the Pumpherston site restoration programme. Some of those considered more interesting and useful are described here. Section 3 outlined where these technologies were used within the overall programme.

4.1 Desk Study

Owing to the site's long industrial history and complexity of operations a comprehensive desk study formed the basis for the two phases of intrusive site investigation. This

involved compiling a large volume of historical information. Aerial photographs were very useful for verifying old site plans. The aerial photographs were viewed stereoscopically so that relief could be examined, allowing estimates of fill thickness to be made. This was used to determine the depths and rates of filling of waste disposal areas. It was also used to assess the increase in the shale bing volumes around the site and hence corroborate estimates of production and waste generation. A second important aspect was to verify the actual site practices. This was achieved by interviews with former workers at the site. These were conducted after the initial desk study information had been assembled so that it could form an *aide memoire*. These interviews allowed insights into the real operations at the site extending back to 1929. However, most information was gathered for the period from 1950. These two aspects of the desk study increased confidence in its validity.

4.2 Investigation of Tar Pond Using Laser Induced Fluorescence CPT

On the basis of the desk study and Phase I investigation information the initial conceptual model indicated that the Golf Course tar 'pond' was potentially a high hazard area. The Golf Course tar pond is located in a former mining area where subsidence of shallow worked seams had created a large void in the ground. This had been back-filled with wastes. Evidence from aerial photography showed the void to be at least 7m deep with an area of some 4,000m^2. It was expected the void was filled with tarry wastes and ash from the site power station. The tars displayed high PAH concentrations. Since PAHs fluoresce strongly in laser light, laser induced fluorescence cone penetrometer testing , LIF CPT, was undertaken to delineate the wastes. A grid of 16 probe holes at 20m spacing penetrated the waste. The LIF CPT was pushed to depths of up to 15m, into the underlying weathered bedrock. The LIF CPT data were validated using the CPT vehicle mounted discrete sampler. The sample intervals were chosen within the tar waste zones by using the LIF data produced on site. Potential advantages of the tool are discussed by Lambson & Jacobs (1995). They include rapid delineation of soil properties and any contamination while minimising human contact. The work also showed that tuning of the laser wavelength for site specific contaminants is important. Interpretation revealed the need to consider all three CPT sensor signals (cone end and sleeve resistance plus fluorescence intensity) when developing a 'signature' for contaminated zones.

The LIF CPT and discrete sampler work allowed characterisation of the Golf Course tar 'pond'. It revealed that the hydrocarbon wastes were incorporated into the void in differing physical states. In the base of the 'pond' the tar was combined with much ash and blaes such that this formed a strong soil skeleton rendering the mixture physically stable. Towards the top of the 'pond' the tar proportion dominates and there is much less ash and blaes. Here the mixture is physically unstable and remedial action is required.

4.3 Tar Properties

A good understanding of both the physical and chemical properties of the tarry wastes was needed in order to assess the associated risks and optimise the remedial action. The characterisation needed to account for the inherent variability in the wastes. This is particularly important when using a risk based methodology to set remedial goals since there is an influence on the confidence levels. On a practical basis, the variability needs to be related to occupational health issues for remediation workers and to material handling. The framework used for understanding the physical and chemical properties of the tarry wastes at Pumpherston is outlined below.

4.3.1 Physical Properties

The physical composition of the tarry wastes can be summarised by considering the relative proportions of hydrocarbon organics (soluble organic fraction, SOF), water and solids. Plotting data for individual samples on a ternary diagram demonstrates three broad waste material types exist. Figure 2 shows the ternary 'lozenges' for these. The three material types are:

1. Wastes with relatively low hydrocarbon and water fractions but high solids contents. These materials are physically stable since the mainly granular soil skeleton carries any overburden loads. They are typical of wastes in the lower part of the Golf Course tar pond and the on site residue ponds.
2. Wastes with a medium level of hydrocarbon and solids fractions but low water contents. These materials are also physically stable. Uphall wastes are typical of these.
3. Waste with relatively high hydrocarbon fractions with low water and solids contents. These materials are physically unstable since the thixotropic tar carries any overburden load. They are typical of wastes in the upper part of the Golf Course tar pond, the Griffiths ponds and the Roman Camp ponds.

4.3.2 Chemical Properties

In terms of chemical properties the hydrocarbons at Pumpherston and associated outlying sites can be divided into two main types, namely, Golf Course and Uphall tar wastes. Some of their properties are outlined in the table below:

Property (Mean Values, w/w)	Material Waste Type	
	Golf Course	Uphall
Soluble Organic Fraction, %	65	29
Solids, %	20	48
Water, %	15	23
Hydrocarbon within SOF,%	16	22
Proportion C10 - C15, %	7	5
Proportion C16 - C22, %	20	61
Proportion C22+, %	73	34
Total PAH, mg/kg	4,400	680
Benzo(a)pyrene, mg/kg	615	63

In deriving the tarry waste chemical properties it was important to understand the exact analytical measurement. For instance, where PAH levels are very high, the standard laboratory methods can under-estimate concentrations due to saturation problems. This can be important since for the Pumpherston waste, the most toxic PAHs accounted for some 12% of the total PAH but contributed over 80% of the risk. The vast majority of the hydrocarbon fraction is judged to be the lower risk aliphatic type. For input to the risk assessment the hydrocarbon fraction was analysed by GC and the results reported in terms of a carbon number distribution, consistent with the groupings of API (1995). Compared with the Uphall type material, the Golf Course tar wastes contain more heavy-end hydrocarbons, with the majority of compounds being C_{20} to C_{30} material, and have higher levels of the more toxic PAHs. These features exclude the bioremediation treatment route. The very low chemical availability of the wastes was corroborated by site monitoring data.

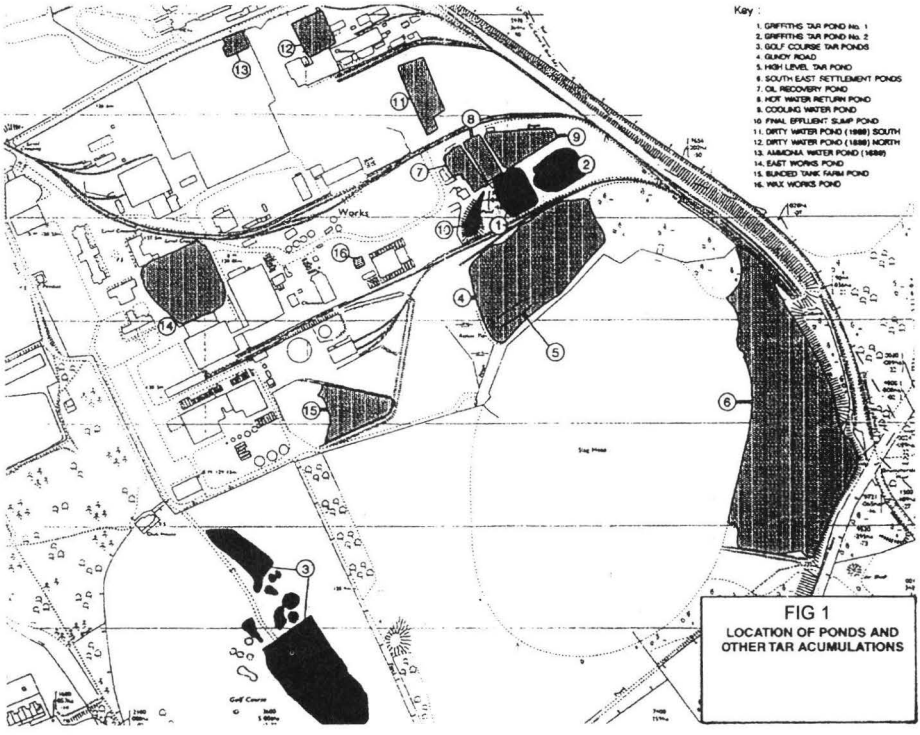
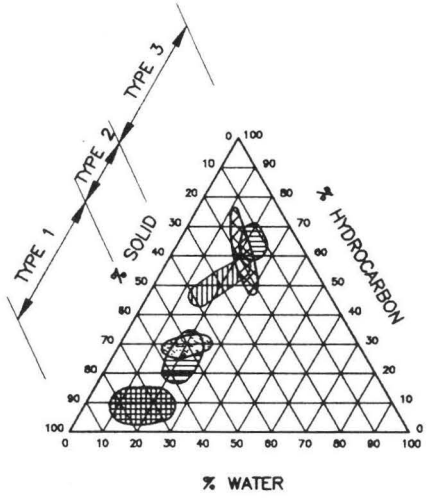


FIG 1
LOCATION OF PONDS AND OTHER TAR ACUMULATIONS



— ROMAN CAMP
— BRICKWORKS
— SITE RESIDUE PONDS
— GOLF COURSE (2 TYPES)
— UPHALL & BRIDGEND

PUMPHERSTON : WASTES TERNARY DIAGRAM

FIG 2

4.4 Site Risk Assessment

The approach combined the historical data and the chemical monitoring results (being the potential contaminant sources) with the groundwater analyses (which gave the potential pathways and flow directions) to estimate migration potential. Qualitative estimations of risk to potential receptors were then made and a conceptual model derived for the site. This model is not regarded as fixed, but evolves to take account of new data. The risk based approach using source, pathway, receptor analysis is consistent with the draft UK statutory guidance for contaminated land (Department of the Environment,1996) and the treatment of risks due to hydrocarbons consistent with CONCAWE (1997).

The background to the conceptual model is the six point restoration strategy for the site as outlined in section 3. There are two main contaminant sources at Pumpherston, surfactants and hydrocarbons. Heavy metals, while present in places at elevated concentrations, were demonstrated an acceptable risk given the proposed end use. Hydrocarbon contamination is present in both the soil and the groundwater. While it is widespread, it is generally concentrated in discrete 'ponds'. It is predominantly high carbon number material with inherently low water solubilities. The majority of the wastes have low hydrocarbon and water fractions and are physically stable. Only where the hydrocarbon fraction is high and the solids content low, is the material physically unstable over long timescales.

The relevant shallow ground conditions at Pumpherston comprise fill over glacial till. They control the migration potential of contaminants. The glacial till is present across the site except where it has been excavated under three 'ponds'. It is an aquitard, limiting the migration potential for the contaminants. Groundwater monitoring data confirm the two primary migration routes identified by site assessment and the geomorphology. Cut-off drains have been installed to intercept both the primary migration pathways. The data confirms the correct positioning of these. Cut-off drain waters are treated in a horizontal flow soil based reed bed system to reduce hydrocarbon and surfactant concentrations to acceptable levels. These measures meet the first two criteria of the restoration strategy.

The elimination of unacceptable risks from tars is effected through remedial works. The physically stable, low hydrocarbon tar ponds can be managed insitu by preventing the direct contact pathways and capturing plus treating any groundwater 'run-off' using the boundary interceptor drains. The hazard assessment reveals that the offsite tar ponds plus the Griffiths and Golf Course tar pond zones (shaded solid on figure 1) require active treatment. Treatment trials show that Uphall type tars can be treated using biological techniques to meet a risk assessed target clean-up level. The Griffiths tars have been stabilised insitu and monitoring has confirmed their physical and chemical stability. It is planned to stabilise exsitu the Golf Course type tar materials in an engineered repository area at Pumpherston which will be capped to prevent the direct contact pathways.

In qualitative terms the site is judged to pose no significant risks (both ecological & health) to the surroundings. Sources and migration routes are understood. The two primary migration routes have been isolated and the produced waters treated. The shallow ground conditions help mitigate the effects of past migration. From monitoring there is evidence of natural degradation of surfactants. The heavier PAHs are generally not available to the groundwater at levels which cause concern.

5.0 Conclusion

The approach used has allowed a complex problem to be simplified. Risk assessment has provided a focus, which together with flexibility and feedback has led to cost optimised remedial solutions. The technologies and decision processes employed will allow a former oil shale refinery and surfactant works to be returned to beneficial use.

The site investigations used a range of techniques, including laser induced fluorescence cone penetrometers. The project has not been afraid to investigate to increase understanding and where appropriate has employed developing technologies. A thorough understanding of the physical and chemical properties of the contaminants identified three material types and associated risks, with each having a different remedial solution. Some 80% of the contamination was dealt with by managing groundwater insitu. This involved 'barrier' cut-off drain installation with treatment for dissolved hydrocarbons and surfactants using a constructed horizontal flow soil based reed bed. Exsitu bioremediation is being used for wastes containing C_{15}-C_{32} hydrocarbon. Insitu and exsitu stabilisation is used for unstable tarry wastes.

Particular emphasis has been given to the role of hazard & risk assessment and interaction with the regulatory authorities during the development of the remediation phases. The biggest beneficial influence in the process has been time. It has enabled options to be assessed, allowing the implications of each to be fully understood before action was taken.

Acknowledgements

The success of the Pumpherston project is being achieved through teamwork. BP acknowledge the efforts of Ove Arup & Partners, Celtic Technologies Ltd, Environment Matters, Keller, I R Robertson & Partners, Oceans Environmental Engineering Ltd, and Waste Management Inc.

References

1. API (1995) American Petroleum Institute Total Petroleum Hydrocarbon Criteria Working Group, *Proceedings 10th Conference on Contaminated Soils,* Amherst, Massachusetts, US
2. Cadell, H M (1913) *The Story of the Forth* , Chapter 11 - The Scottish Mineral Oil Industry, Published Maclehose & Sons, Glasgow
3. CONCAWE (1997) European Oil Industry Guideline for Risk Based Assessment of Contaminated Sites, Report 2/97, CONCAWE, Brussels
4. Department of the Environment (1996) Consultation on Draft Statutory Guidance on Contaminated Land, DoE, London, September 1996
5. Lambson M D & Jacobs P A (1995) The Use of Laser Induced Fluorescence Cone for Environmental Investigations. *Proceedings of the International Conference on Cone Penetration Testing, CPT'95,* Linkoping, Sweden
6. Pollard S J T, & Herbert S M (1998) Contaminated Land Regulation in the UK: The Role of the Environment Agency and Scottish Environment Protection Agency *6th International FZK/TNO Conference on Contaminated Soil,* Edinburgh, UK

Index of keywords

β-cylodextrin, 1207
1-hydroxypyrene, 1005
abandoned waste disposal sites, 681, 829, 891
acid-mine drainage, 1223
adsorption, 585, 879, 925, 981, 997, 1087, 1139
agriculture, 453, 793, 961, 1043, 1105, 1157
air migration, 1107
alfalfa, 1041
ammonia, 855
anaerobic, 513
analytical methods, 83, 791, 841, 847, 871, 895, 901, 913, 927, 947, 1015, 1057
aquifer, 143, 571, 1121, 1195, 1229
aquifer A, 793
aromatic hydrocarbon contamination, 575, 905, 1185
aromatic hydrocarbons, 101, 109, 181, 435, 549, 811, 835, 863, 887, 1183
arsenic, 321, 873, 961, 1195
assessment risk, 963, 965
atmospheric deposition, 851
authorities, 19, 25, 661, 723, 733
authorities' role, 33, 51, 61, 403, 445, 495, 691, 725, 761, 777, 1045
availability, 453, 847, 1123, 1177
background levels, 783, 1013
bacteria, 337, 919, 933, 935, 959, 1121
barriers, 109, 941, 1055, 1065, 1087, 1097, 1121, 1203
Basque Country, 1263
behaviour of contaminants, 213, 495, 821, 825, 831, 849, 953, 955, 969, 971
bentonite-cement, 1065
benzene, 109, 843, 1029
bioassays, 345, 355, 759, 1001, 1039, 1051, 1109, 1201
bioavailability, 123, 133, 251, 321, 453, 531, 789, 791, 797, 865, 889, 923, 961, 991, 1039, 1085, 1189
biodegradability, 251, 791, 95, 133, 795, 805, 835, 923, 935, 949, 959, 1035, 1043, 1071, 1149, 1185
biogradation, 797
biological processes, 1131
biological tests, 1115
biological treatment, 251, 403, 531, 1073, 1289
biomonitoring, 905, 1025, 1109
bio-piles, 403, 1091
bio-reactor test, 531, 1091
bioreactors, 531, 1071, 1091, 1177, 1189
bioremediation, 95, 143, 403, 495, 513, 523, 571, 599, 609, 821, 915, 925, 967, 995, 1051, 1091, 1119, 1155, 1187, 1197, 1207
biosensors, 123, 839, 923
biosurfacant, 995
biotest, 1041
biotoxicity, 1123
BTEX, 203, 835, 839, 863, 887, 911, 1121
buffering capacity, 851
buildings, 641, 1219
cadmium, 445, 609, 865, 993, 1023, 1025, 1195, 1201
carbon balance, 531, 855, 863, 1091
carbon tetrachloride, 843
case history, 143, 571, 1187
case study, 9, 65, 445, 725, 867, 967, 983, 1029, 1069, 1289
catcher sand, 1101
cement, 1135
cement-bentonite, 641
characterization, 213, 251, 491, 807, 825, 827, 835, 901, 907, 935, 945, 951, 999
chemical oxidation, 1189
chemical speciation, 123, 173, 897, 927, 977, 979, 1093
chemical treatment, 479, 539, 549, 813, 1057
chemico-physical processes, 1131
chlorinated hydrocarbons, 109, 143, 191, 435, 549, 571, 869, 885, 903, 911, 941, 1009, 1059, 1071, 1079, 1121, 1123, 1141, 1149, 1187, 1221, 1999
chromium, 865, 873, 925

classification, 221, 479, 743, 757, 1075, 1083
clay, 413, 453, 561, 807, 825, 903, 967, 1087
clay liner, 1055
clean up, 1105
clean-up cost, 61, 723, 771, 823, 1173
clean-up operation, 1079
clean-up technologies, , 9, 25, 383, 575, 691, 723, 809, 823, 925, 1075, 1083, 1129, 1143, 1145, 1189, 1225, 1273
collateral risks, 711
complexing agents, 1137
compost, 1149
compressive strength, 1135
computer model, 621, 759, 793, 815, 907, 1027, 1045, 1193
computer simulation, 943, 1035, 1087, 1143
concerted action, 19, 25
conditional simulation, 1013
construction design, 585
contact biotest, 1207
contaminated land, 775, 1219
contaminated plume, 173, 413, 815, 1001
contaminated site investigation, 1263
contaminated site remediation, 1263
contaminated sites, 19, 25, 75, 163, 301, 367, 491, 495, 641, 651, 671, 681, 701, 729, 731, 733, 743, 757, 767, 771, 793, 801, 815, 935, 875, 1009, 1027, 1033, 1035, 1057, 1129, 1163, 1215, 1227, 1253, 1263, 1273
contaminated soil administration, 661, 761, 1191
contaminated soil, 251, 321, 337, 355, 403, 471, 479, 531, 539, 609, 621, 753, 759, 765, 781, 807, 813, 821, 825, 831, 833, 837, 847, 849, 861, 865, 875, 893, 897, 899, 901, 907, 913, 915, 953, 955, 967, 983, 1005, 1021, 1025, 1031, 1037, 1039, 1049, 1059, 1075, 1085, 1091, 1095, 1105, 1109, 1111, 1119, 1131, 1145, 1161, 1175, 1187, 1221, 1225
contractor responsibility, 725
co-oxidation, 919
copper, 865, 1025, 1085
copper ion, 1161
cost-benefit analysis, 221, 651, 803, 1113, 1141, 1153, 1173
costs, 691, 1193, 1205, 1253, 1273
covering system, 1211
credit approval process, 711
crops, 1155
cyanide, 819, 1073, 1099
cyclodextrin complexation, 1207
data analysis, 213, 725, 771, 815, 951, 987, 1019
databases, 621, 759, 907, 1083, 1019, 1069, 1163
decision support system, 1169, 1173, 1193
decontamination, 661, 1137, 1143, 1179
decontamination techniques, 9, 461, 495, 813, 1083, 1205
deep compaction, 967
degradation, 413, 585, 903, 941, 1219
derelict land, 1263
dermal absorption, 1031
desorption, 561, 857, 981, 997
DHS from composts, 909
diesel, 883, 995
diffusion, 231, 981
dioxins, 539, 915
disposal sites, 1181
dissolved organic carbon (DOC), 909, 981
distribution coefficient, 173, 879, 881, 953
DOC (see dissolved organic carbon)
drainage, 937
dredged material, 805, 1135, 1181, 1193
drums, 1177
due diligence, 705
dumping site, 893
dump-site monitoring, 1055
earthworms, 1047

ecological effects, 337, 445, 651, 781, 829, 883, 1043, 1089, 1175
ecosystems, 337
ecotoxicity, 1041
ecotoxicological tests, 959
ecotoxicological, 345, 759, 797, 935, 1039, 1201
ecotoxicology, 1051
education and training, 721, 771, 1213
electrodecontamination, 1161
electroextraction, 1161
electrolysis, 1093, 1123, 1133
encapsulation, 1089
environment desk corporate banking, 711
environmental effects, 1193
environmental impact, 153, 367, 681, 845, 1095, 1141, 1173, 1205
environmental investigations, 691, 721, 725, 777, 807, 901
environmental management, 61, 367, 621, 651, 701, 725, 1069, 1113, 1153, 1191
environmental policy instruments, 51, 163, 291, 367, 661, 743, 761, 767, 1069, 1083, 1227
environmental policy, 681
environmental risks, 291, 705, 791, 851, 1009, 1229
environmental technology, 771, 807, 877
ethanol, 843
European Union, 19, 25
examination, 191
excavation, 1057, 1221, 1229
expert systems, 957
experts for environmental contaminations, 887
explosives, 311, 513
exposure, 321, 749, 781, 1005, 1031, 1037, 1049, 1067
exposure model, 301, 311, 1019, 1045
exposure pathway, 1037, 1049
extensive remediation concepts, 191
extractability, 797
extraction, 889, 955, 1059, 1093, 1123, 1133, 1151, 1189, 1999
fertilization, 609, 855
fertilizer, 1157
fiber-optic sensor technology, 911
field experiment, 337, 781, 1043, 1065, 1095, 1175
field injection experiment, 101
field study, 805
field test, 143, 571, 771, 911, 917, 1159, 1187
fine particles, 479, 877, 879, 927, 1075, 1189
firing range, 1101
fixation, 955, 1205
flocculation, 113
flotation, 479, 1075
flow-field-flow-fractionation, 279
fluidized-bed reactor, 1103
fluorescence detection, 279
functional layers, 993
fundamentals and evaluation criteria, 1131
gas chromatography, 913, 997
gas emissions, 539
gasworks, 425, 495, 791, 819, 917, 1073, 1189
genetically engineered microorganisms (GEMs), 839
genotoxicity, 355
geoelectrical measurements, 807
geoelectrics, 1159
geophysical methods, 495, 807
geostatistics, 1013
government, 9, 1227
governmental, 1127
governmental directives, 377, 745, 785
groundwater, 109, 765, 815, 819, 845, 919, 1035, 1063, 1117
groundwater and soil contamination, 887
groundwater clean-up, 95, 413, 571, 779
groundwater flow, 831
groundwater modelling, 829, 943, 1067
groundwater monitoring, 621, 681, 815, 911, 929, 1065
groundwater protection, 393, 445, 731

groundwater remediation, 143, 435, 571, 885, 1061, 1121, 1165, 1203, 1289, 1999
groundwater sampling, 435
groundwater treatment, 425, 1071, 1073, 1195, 1273
guide levels, 1129
guidelines, 109, 291, 311, 723, 755, 765, 769, 803, 1019, 1063, 1141, 1215
halogenated hydrocarbons, 143, 413, 571, 887, 1183, 1187
hazard ranking, 773, 1001, 1019
hazardous goods, 887
hazardous waste, 1205
HCH (see hexachlorocycohexanes)
health and safety, 751, 769
health risk, 291, 1089
heavy metals, 123, 461, 471, 479, 609, 759, 779, 785, 807, 817, 841, 847, 851, 865, 897, 899, 907, 927, 937, 955, 961, 963, 965, 975, 991, 1051, 1085, 1089, 1093, 1101, 1105, 1111, 1115, 1119, 1123, 1133, 1137, 1139, 1145, 1195, 1205
heterogeneity, 827, 969
hetero-PAH, 871
hexachlorocycohexanes, 109, 893, 1151
historical investigation, 773
homogenization, 827, 1177
housing, 671
human health risk, 75, 301, 321, 445, 753, 765, 1013, 1019, 1027, 1031, 1037, 1045, 1049
human-toxicological, 1069
humic acids, 279
humic substances, 113, 821, 931, 1177
hydrocarbons, 75, 95, 241, 403, 531, 719, 883, 899, 909, 911, 1009, 1023, 1051, 1067, 1091, 1095, 1141, 1177
hydro-colloids, 279
immobile zones, 231
immobilization, 599, 821, 855, 941, 1099, 1201
impermeable industrial flooring, 745
incineration, 851, 1205
industrial areas, 651, 723, 1227
industrial sites, 691, 701, 743, 745, 1063, 1169, 1171, 1215
in-situ, 995, 1203
in-situ air sparging, 1107
in-situ bioremediation, 109, 113, 143, 181, 191, 367, 403, 435, 571, 811, 835, 839, 863, 935, 1067, 1085, 1117, 1121, 1145, 1187, 1225
in-situ groundwater remediation, 203, 231, 585, 969, 1097
in-situ measurement technique, 807, 837, 911, 989
in-situ methods, 377
in-situ microcosms, 101
in-situ remediation, 425, 561, 575, 599, 909, 1021, 1061, 1095, 1139, 1141
in-situ treatment, 9, 1175, 1201
intelligent soil, 491
international cooperation, 729, 731
intervention value, 781
intervention values for remediation, 1253
intervention values for soil clean up, 759
inventory, 767, 867, 1221, 1263, 1273
investigations, 711
ion-exchange membrane, 1161
ion-exchange resin, 897, 1161
isolation, 931
isotope hydrology, 867, 929
isotope methods, 821, 891, 955
knowledge transfer, 9, 19, 25, 725, 733, 745, 1045, 1083, 1163, 1213
laboratory batch experiments, 101
land register, 705, 767, 1215, 1227
landfill gas, 153, 641, 1229
landfill leachate, 153, 1001, 1229
landfill site, 1215
landfills, 445, 621, 661, 1211, 1263
large-scale experimental basin, 575, 969
laser light scattering, 279
laws, 1009
leachates, 173, 925, 1223

leaching behaviour, 791, 851, 909, 1093, 1123
leaching, 461, 897, 1099, 1179
lead, 321, 461, 847, 955, 975, 1013, 1089, 1115, 1179
legislation, 33, 43, 621, 661, 671, 691, 705, 725, 767, 1045, 1227, 1253
liability, 51, 61, 661, 705, 729, 1009, 1227, 1253
life-cycle assesment, 367, 1069, 1193
life-cycle impact assessment, 1069
limiting values and standard, 691, 1147
management, 61, 65, 771, 1011, 1221
manure, 855
mapping, 1013, 1113
marine, 995
mass spectrometry, 913
mass transfer calculations, 863
mass transfer, 133
mass transport calculation, 1191
mass transport, 231
mathematical models, 813
mercury, 173, 865, 1123, 1133, 1195
metabolites, 871
metal, 337, 837, 947, 1201
microbial activities, 337, 883, 891, 899, 1149, 1155, 1157, 1197
microbial degradation , 109, 919
microbiological degradation, 435, 811, 893, 905, 931, 1177
microbiological parameters, 345
microbiological soil remediation, 531, 751, 933, 1091
microcosms, 513, 795, 959, 1117
micro-organisms, 337, 835, 865, 935, 1015, 1157, 1203
migration, 825
military sites, 311, 1253
mine tailings, 937
mine waste, 1223
mineral oil, 75, 251, 811, 879, 907, 1073
mineral oil hydrocarbons, 833, 1103
mining, 681, 749, 955, 979
mixed population, 1103
mixed wastes, 1147
mobility, 173, 241, 817, 849, 927, 961, 1085, 1139
mobilization, 963, 965
model, 1005
modelling, 719
modelling of ground water flow, 1229
models, 1049, 1113, 1127, 1141
monitoring, 153, 321, 785, 795, 839, 845, 869, 907, 987, 989, 1063, 1111, 1211, 1223
monitoring procedures, 383, 745, 809, 869, 895
MTBE, 919, 1067
naphthalene, 949, 999, 849, 997, 1029
national binding values, 43
national law, 749, 777, 1273
national programmes, 681, 1273
natural attenuation, 95, 101, 109, 143, 181, 191, 203, 491, 571, 795, 805, 811, 819, 829, 995, 1029, 1067, 1121
natural biodegredation, 191
nickel, 977, 981
nitrate, 855, 863, 1117
nitrogen, 609, 855, 1197
nodulation, 1041
non-isothermal transfer, 843
occupational safety, 751, 769
off-site treatment, 9, 1075
oil products, 75, 495, 795, 1157, 1197, 1095
oil-contaminated soil, 1207
on-site treatment, 9, 65, 403, 723, 805
organic chorinated compounds, 539
organic compounds, 1177
organic contaminants, 599, 785, 825, 919, 941, 1001, 1039
organic contamination, 95, 1165
organic matter, 837, 903, 927, 1157
oxidation, 1123, 1133
ozone, 1073
PAH (see polycyclic aromatic hydrocarbons)
partitioning, 857, 881, 1087
PCB (see polychlorinated biphenyls)
PCBs dechlorination, 523
PCDD/Fs, 539, 1205, 1273

pesticide (HCH), 163
pesticide transport, 941
pesticides, 109, 549, 893, 1043
petroleum hydrocarbons, 75, 203, 845, 1077, 1121, 1143, 1159, 1191
phenanthrene, 999
phenols, 113, 181, 841
phosphorous, 1057
photoacoustic spectroscopy, 999
physical states, 133
physico-chemical processing, 837, 1073, 1093, 1123, 1133, 1189
physico-chemical washing process, 877, 1095
phytoremediation, 939, 1105
phytotoxicity, 345, 967, 1155
piling, 1229
pilot plant, 1073
pilot test, 65
planning, 311, 769, 1227
plant, 1221
plants, 453, 609, 823, 939, 955, 961, 1111, 1119, 1201
plume, 829
policies, 61, 729, 731, 829, 1273
policy, 621
pollutant transport, 817
pollution prevention, 1169
polychlorinated biphenyls, 539, 959, 1079
polycyclic aromatic hydrocarbons, 113, 133, 213, 241, 403, 413, 425, 789, 791, 797, 805, 821, 825, 831, 833, 849, 857, 871, 885, 889, 905, 907, 909, 917, 1005, 1041, 1051, 1073, 1075, 1189, 1289
polynuclear aromatic hydrocarbons, 935
porosity, 1135
porous media, 813
practice, 61, 621, 1129
prevention policies, 33
prevention, 61, 745, 751, 769, 855, 1015, 1147, 1171
priority lists, 773, 1083, 1215
priority sites, 757
priorization, 1263
program, 1215
programme of research, 19, 25, 771, 1077
prosecution, 777
protection, 621, 1019, 1171, 1175
psychological aspects, 291
public, 1163
public awareness, 393
public safety, 1019
pumping, 231, 885
purification of exhaust air, 1165
QA/QC program, 895
quality assurance, 383, 745, 763, 809, 895, 901, 947, 1011
quality control, 221, 383, 861, 895, 947, 1011, 1129
quality of the soil, 83, 783, 785, 901, 975, 977, 1109, 1201
quality standards, 383, 763, 779, 809, 1033, 1147
radioactive contamination, 749, 973, 1113
radionuclides, 931, 973, 1047
ranking system, 291, 757, 1083, 1147, 1171
reactive barriers, 585
reactive solutes, 993
reactor, 491, 1075, 1097
real estate, 671, 701
recycling, 65, 1101
redevelopment, 661, 1229, 1227
redox conditions, 279
refinery site, 75, 863, 1289
regeneration, 33, 65, 721, 1227
register, 1253
regulation, 751
regulations, 749, 755, 761, 765, 1019, 1163
reliability sampling, 221
remedial action concept, 393
remedial action scenario, 1089
remedial action techniques, 367, 377
remedial investigation, 43
remedial measures, 43
remediation, 1, 9, 311, 425, 461, 641, 651, 661, 681, 753, 755, 873, 893, 935, 979, 979, 1035, 1051, 1057,

1079, 1115, 1127, 1129, 1143, 1153, 1175, 1185, 1219, 1223
remediation concept, 491, 749, 1061, 1069, 1083, 1203
remediation efficiency, 9, 383, 809, 863, 959
remediation plan, 43
removal rates, 403, 561, 969
responsibility, 661, 761
reuse, 651, 721, 749, 1057, 1101, 1211
reuse (of sites), 691, 701, 753, 771, 1089, 1229
rhizobium, 1041
risk analysis, 19, 311, 691, 711, 745, 977, 979, 1109, 1221
risk assessment, 19, 25, 75, 291, 321, 425, 743, 751, 753, 755, 765, 769, 773, 781, 801, 803, 815, 821, 943, 957, 1005, 1009, 1011, 1013, 1015, 1019, 1023, 1027, 1029, 1031, 1035, 1037, 1039, 1045, 1049, 1051, 1067, 1089, 1169, 1171, 1173, 1253
risk communication, 775
risk management, 51, 61, 75, 291, 609, 705, 729, 731, 753, 1009, 1127, 1147, 1289
risk, 291, 495, 781, 1009
risks, 109, 641
samples, 861, 875
sampling methods, 221, 827
sampling programme, 383 ,809, 945
sampling strategies, 801, 867, 869, 945, 987
sampling techniques, 435, 827, 885, 1043
sampling theories, 803, 875
scientific principles, 1131
screening, 479, 881, 913, 1001
sediments, 113, 523, 805, 935, 941, 1075, 1193
sequential extraction procedure, 939, 961, 1093
simulation model, 813, 1143, 1181
site investigation, 83, 173, 763, 801, 807, 815, 891, 937, 957, 1215
site management, 711
site restoration, 651
sludge, 453, 857, 1135, 1139, 1155, 1181
sludge/slurry, 1095
slurry bioreactor, 513
slurry wall, 1087
slurry, 531, 893, 983
sodium chloride, 1179
sodium humate, 1179
software tool, 367, 755, 801, 1069, 1163
soil, 279, 321, 345, 461, 513, 523, 817, 819, 871, 881, 889, 903, 905, 917, 923, 931, 935, 987, 997, 1037, 1099, 1171, 1179
soil air, 869, 1063
soil and groundwater contamination, 61, 75, 163, 213, 691, 755, 771, 779, 835, 839, 971, 1229
soil clean-up criteria , 75, 1037, 1049
soil clean-up, 599, 779, 915, 1191, 1187
soil contamination, 849, 961, 1183
soil elution/extraction methods, 241
soil erosion, 867, 1175
soil fauna, 883, 1039, 1043, 1047
soil gas, 869, 989
soil moisture, 1055
soil permeability, 831
soil properties, 83, 491, 899
soil protection policy, 745, 781
soil protection technology, 745
soil protection, 1, 729, 731, 1063, 1147, 1169, 1253
soil remediation, 377, 471, 729, 731, 877, 879, 997, 1083, 1101, 1111, 1137
soil toxicity, 1207
soil vapour extraction (SVE), 367, 413, 561, 575, 1067, 1143, 1165, 1183
soil vapour, 1999
soil washing, 65, 425, 479, 873, 877, 907
soil/plant transfer, 873, 977, 979
soil-to-plant transfer, 609
soils decontamination, 719
solidification, 1135

solidification/stabilization, 1289
solvency risks, 711
solvents, 413, 789, 967, 1059, 1095, 1151
sorption, 113, 789, 849, 881, 935, 1201
spatial variability, 987, 1013, 1111
stabilisation, 1115
stabilized waste, 851
standardization, 83, 841
statistics, 801
steam stripping, 575
sulphates/sulfates, 983, 1219
sulphides/sulfides, 479, 937
support, 1215
suspected areas, 773
sustainability, 495, 661, 1019, 1153
sustainable soil use, 1, 445, 729, 731
symbiosis, 1041
target value, 753, 755, 781, 783, 785, 1067, 1147
temperature, 561, 575, 933
test values, 1183
thermal desorption, 561
thermal treatment, 561, 789, 813, 1079, 1101, 1205
thermodesorption, 539, 599, 1093
thin-layer chromatography, 833
toluene, 933
toxic metabolites, 959
toxic metals, 1021
toxicity decontamination, 1115
toxicity potential, 241
toxicity tests, 1039, 1109
toxicity, 321, 355, 923, 933, 1001, 1069
tracer, 969
transport in soil, 849
transport modeling, 993
treatment, 513, 1129, 1135
treatment methods, 1193
treatment policy, 661
trichloroethene, 1097
trichloroethylene, 109, 143, 561, 571, 969, 1187
trigger values, 291, 311
trinitrotoluene, 241, 939
unsaturated soil, 843, 993
unsaturated zone, 575, 817
urban areas, 701, 975, 1155
USTs, 1023
utilization concept, 701
UV oxidation, 549, 1073
vacuum, 719
vacuum extraction, 413, 425, 1143
vadose zone, 1187
vadose zone monitoring, 1159
values, 671
vegetation, 153, 1211
volatile organic compounds (VOCs), 779, 869, 885, 887, 1009, 1143, 1183,1221
volatile organochlorines, 1107
volatilization, 561, 599
warfare-related contaminated sites, 311, 773
washing stage, 1189
waste disposal sites, 929, 943
waste disposal, 1055
waste minimization, 1019
waste processing, 425, 1133
waste water treatment, 549, 925
waste water, 793, 905, 911
water balance, 1211
xenobiotic, 849, 923
zinc, 337, 445, 479, 609, 975, 983, 1023, 1025, 1195, 1201

Index of authors

Abbott A., 1203, 931
Adler R.R., 163
Al-Awadhi N., 1095
Al-Daher R., 1095
Al-Dhahair Z., 1079
Al-Dhahir F.M., 413
Alekseev A.N., 1175
Alekseyev M.A., 1157
Allen J., 331
Alphenaar A., 191
Al-Saleh E., 835
Alsaleh E.S., 935
Alsberg T., 261
Altmann S., 817
Alvarez A., 1263
Ammerlaan R.A., 723
Ampleman G., 513
Anderson B.N., 839, 865
Anderson G.K., 983
Andreotti G, 403
Apak R., 1179
Appelman J.J.M., 1073
Argus R., 383
Argyraki A., 221
Arkhipchenko I.A., 1155, 1157
Arlotti D., 403
Arnold S.M., 1031
Asada M., 1095
Aston S., 775
Aurrecoechea J.L., 1263
Ávila P.F., 937
Baartmans R., 109
Babel W., 893
Bagó T., 1051
Bakker S., 1201
Bakker T., 1193
Balba M.T., 1095
Balderer W., 891
Bannick C.G., 83
Barančíková G., 903
Baranger P., 817
Barbafieri M., 977, 979, 1139
Barbé P., 825
Barbolina I.I., 1155
Barbosa-Jefferson V.L., 123
Barczewski B., 969, 1249
Bardos P., 729, 733
Bardos R.P., 771
Barna L., 849
Bartell S., 1049
Bartlett C.L., 571
Bär E., 835, 839
Battermann G., 367, 863, 1069
Battisti A., 1103
Bauer S., 1071
Bauman B.J., 971, 1077
Baumann A., 955
Baun A., 1001
Bayard R.M., 849
Beaulieu M., 51
Bech-Nielsen G., 471
Becker K., 1103
Becker P.-M., 599
Becker P.M., 113
Beitinger E., 585
Belic A., 793
Belic S., 793
Bell M.J., 61, 143., 571, 727, 1187
Bender A., 367, 1069
Bennett A.M.A., 917
Berbenni P., 1185
Berendsen T., 621
Bergmann V., 1057
Bermond A., 1021
Bestetti G., 949
Betz C., 575
Beurmanjer C.A., 1007
Bicanic D., 999
Bieber A., 1235
Bielek P., 991
Bierkens J., 1109
Bilbao V., 1149
Birnstingl J.G.A., 1079
Birnstingl J., 311
Bispo A., 355
Bjerg P.L., 101, 1001
Blackmore J., 1999
Blackmore K., 845, 1165
Blánchet D., 791
Blazquez J.C., 1263
Boag B., 883
Bode-Kirchhoff A., 1041
Boehringer A., 1057
Boggs J.M., 95

Böhme P., 1057
Bonilla A., 1143
Bonten L.T.C., 789
Bosma T.N.P, 109, 197
Bourgois J., 1019
Boutouil M., 1135, 1181
Braithwaite P.A., 1229
Brandelik A., 1055
Braun J., 969
Braun R., 797
Breiter R., 879
Bretzel F., 975, 1139
Breure A.M., 133, 337
Brohon B., 899
Bronders J., 757
Browne M.J., 1013
Bruning H., 1075
Bryniok D., 1071
Buchanan R.J., 571
Bunge A.L., 1031
Bunge R., 875
Bürck J., 911
Burmeier H., 585
Butovsky R.O., 1025
Buzzelli M., 1159
Calmano W., 847, 941, 1093
Camiña I., 1263
CARACAS, 25
Carlier M., 831
Carrier M., 807
Cartmell E., 1117
Ceenaeme J., 757
Ceenaeme J., 767
Cerretti R., 691
Chablain P.A., 933
Chapelle F.H., 143
Charbonnier P., 817
Chiampo A., 181, 1023
Christensen T.H., 101, 561, 1001
CLARINET, 25
Clark L., 1117, 1165, 1185
Clark T.R., 539
Cohrs I., 531
Collina E., 951, 949, 1033
Colomer V., 1221
Conil P., 1181
Corbisier P., 1109
Corcho D., 919
Cork J., 65
Cornelis C., 757, 759, 993
Cornu S., 817
Correll R.L., 453
Cortet J., 1043
Couper A.S., 495
Couturier D., 913
Crabb D., 883
Crawford R.L., 75
Crout N., 123
Crowther Y., 775
Cuesta P., 1143
Cummins D.I., 153
Cuypers M.P., 999
Dab W., 753, 1005
Dadea C., 979
Dalmacija B., 793
Daly P.J., 1065
Darmendrail D., 743
Davies J.W., 143
Davis J.M., 571
Davison W., 123
de Boer C., 1007
de Groof A.A., 763
de Koning W., 763
de la Quintana E., 1151
de Leeuw R., 999
De Nijs W., 767
de Vries P.W., 1073
de Weger D., 1169, 1171
Dearlove J.P.L., 1203
Deckwer W.-D., 1177
Deigaard L., 1141
Delolme C., 899
Delorme P., 831
Denner J., 733
Dettwiler J., 1253
DeWeerd K.A., 571
Díaz A.I., 1149, 1151
Dijkmans R., 1083
Dock L., 321
Doddema H.J., 109
Doetsch P., 301, 651
Dóka O., 999
Donner A., 915
Dor F., 753, 1005

Dreschmann P., 809
Dries V., 1083
Druelle V., 791
Dück J., 879
Ducrocq V., 959
Dudermel P.M., 913
Duffy C., 839
Duncan H., 883, 1119
Duncan H.J., 549, 925, 947, 1225
Duong V.-L., 1019
Dupeyron S., 913
Dupuy N., 837
Duresch R., 1057
Eggels P.G., 1193
Egusa N., 1107
Ei T.A., 143
Einsele G., 881
Elkenbracht E., 729
Ellis D.E., 143, 571, 727
Emmerson R.H.C., 413
Empereur-Bissonnet P., 753, 1005
Enfield C.G., 561
Engelhardt D., 723
Epelde J., 1263
Eschenbach A., 821
Evans J.C., 1087
Fairley M.A., 927
Falkenberg J.A., 985
Fallick A.E., 929
Färber A., 575
Farmer J.G., 927, 929, 931
Feige-Munzig A.P., 769
Fenwick C., 835
Fenyvesi E, 1207
Ferguson C., 19, 311
Ferguson C.C., 801, 803, 945, 1013
Ferguson Y., 923
Ferruti L., 691
Ferse W., 957
Filauro G., 403
Flagg J., 203
Fleischmann S., 345
Fleming G., 943
Flowers T.H., 549, 721, 925, 947
Folkard A.M., 153
Folkerts A.J., 337
Formisyn P., 1019
Forster V., 775, 895, 901, 1061
Förstner U., 279, 851, 941, 981
Franke S., 1123
Franken R.O.G., 785
Franz T., 1187
Franzius V., 19, 1233, 1235
Frauenstein J., 681
Freier K., 43, 301, 1235, 1241
Fukumorita T., 779
Fukuura K., 1107
Galera J., 1263
Gallagher W.E., 539
Gälli R., 1067
Gannon D.J., 727, 1187
García-Rizo C., 965
Gardner M.J., 861
Garlock T., 1037
Gartner M., 797
Garvin S.L., 641, 1219
Gavach C., 1161
Gavinelli M., 1159
Gawlik M., 1009
Gehrke M., 585
Geiger W., 957, 1163
Gergel'ová Z., 903
Gerritse J., 197
Gerth J., 873, 981
Geuzens P., 757, 993
Gevaerts W., 1083
Gil M., 963
Giles D.P., 1027
Gilot P., 719
Globus A.M., 843
Gloeden E., 163
Glover L.A., 839, 865, 923
Goldsborough D.G., 725, 1045
Golosov V.N., 867
Gong P., 345
Goodfellow J., 1205
Gordon J.E., 1
Gorostiza I., 1149
Gould J., 721
Gourdon R., 849
Goyvaerts M.P., 759
Graham M.C., 931
Grant C.D., 453
Grathwohl P., 881

Green C.M., 575
Grieve I.C., 1223
Griffioen J., 231, 811
Grimski D., 651
Groboillot A., 933
Groenwold J., 989
Grotenhuis J.T.C., 789, 989, 999
Gruiz K., 1051, 1207
Grünhoff D., 301
Güçlü K., 1179
Guerin P.M., 967
Guerin T.F., 967, 995
Guespin-Michel J.F., 933
Guillaume B., 1019
Guiot S.R., 513
Gupta S.K., 1085
Guy R.H., 1031
Haemers J., 823
Haeseler F., 791
Haider I., 835
Haigh D.G., 1097
Hall D.H., 1035
Hallier-Soulier S., 959
Halliwell M., 1219
Hansen H.K., 471
Hansen L., 471
Hanson G.J., 571
Harkes M., 109
Harkness M.A., 571
Harmsen J., 805
Harris M.R., 945, 1011
Harris R.C., 755, 1035
Harrison A., 967
Hartless R., 641
Hassen-Khodja D., 1161
Hawari J., 513
Heal K.V., 1223
Heasman L., 895, 901
Heidenstam O., 261
Heijer R., 631
Heitkamp M.A., 571
Heitzer A., 1191
Hempfling R., 301
Henkler C., 835
Henkler R., 835, 839
Henkler R.D., 865
Herbert S., 33, 755, 1153
Heron G., 561
Hetterschijt R.A.A., 231
Heuel-Fabianek B., 383, 809
Hierro B., 1143
Hipkin J.A., 1223
Hirata T., 1107
Hirschmann G., 851
Hizal J., 1179
Höll W.H., 1137
Holmes M.W., 143, 571, 1187
Holton I.R., 1065
Holzwarth F., 1233
Holzwarth W., 1263
Hommelgaard H., 819
Honders A., 907
Hoogewerff J., 955
Hooker P.J., 1013
Hoppener C., 731
Hübenthal K.-H., 1245
Huebner C., 1055
Huffman G.L., 539
Hund K., 241, 909, 1039
Hupe K., 531, 1091
Hurtig H.-W., 367, 1069
Huttula P., 1273
Huvenne J.P., 837
Hwu C.S., 989
Ivanova N.N., 867
Iwabuchi M., 1095
Jäger P., 701
Jaggy M., 711, 1253
James R.E., 855, 1147
James S.C., 9
Jamet Ph., 213
Janssen R., 1173
Jardine F.M., 413
Jauzein M., 355
Jefferis S.A., 1061, 1097
Jeffries R., 775
Jeffries R.A., 883
Jernej J., 1103
Johannsen J., 1183
Johnson S., 729, 771
Jones K.C., 889
Jones S.D., 917
Jordan P., 891
Jørgensen K.S., 261, 915

Josef R., 969
Jourdain M.J., 355
Joziasse J., 1193
Kähkönen L., 1197
Kalevi K., 261, 915, 1273
Kammer F.v.d., 981
Kampbell D.H., 1187
Kämpfer P., 905
Kamsma T., 829
Karstensen K.H., 261, 897
Kasamas H., 19, 733
Kaukal B., 773
Kayser A., 1111
Keijzer Th.J.S., 857
Keller A., 1111
Kemp R., 775
Kennedy C., 113
Kern A., 383, 809
Kerr J., 1119
Keuning S., 491
Kiayias G., 173, 1067
Kibblewhite M., 895, 901
Kiefer R., 1137
Kiefhaber K.P., 701
Killham K., 123, 839, 923
Kissel J., 1037, 1049
Kissling O., 891
Kiviranta H., 915
Kjeldsen P., 819
Klecka G.M., 143, 571, 727
Klein G., 1109
Kliem B.K., 471
Klier N.J., 143
Klöpffer W., 367, 1069
Klöppel H., 909
Knackmuass H.-J., 1071
Koenigsberg S.S., 1121
Kögel-Knabner I., 953
Kohler W., 367, 1069
Kohlmeier E., 435
Koivunen M., 1197
Kok A.P., 811
Kok T., 377
Kolb W., 701
Koning M., 531, 1091
Kontopoulos A., 461, 1115
Koopal L.K., 1075
Kopinke F.-D., 599, 997
Kopinke F.D., 113
Kopponen P., 1089
Kördel W., 241, 909
Korthagen E.J., 777
Koschitzky H.-P., 575, 969, 1249
Köster R., 921
Kotte G., 1057
Kovalick jr W.W., 9
Koziollek P., 1071
Kramer K., 911
Kramer Th.J., 1101
Kramm U., 955
Krishnan E.R., 539
Kukkamäki M., 1273
Kumamoto S., 1095
Kvasnikova E.V., 973
Kyas A., 711, 1253
Laidler D., 771
Lambson M.D., 1289
Lamé F.P.J., 783
Langdon N.J., 1027
Larranaga E., 1263
Lasagni M., 949, 951, 1033
Le Hécho I., 817
Leberer A., 873
Lecomte P., 825, 827
Lee P.H., 1205
Leenaers H., 783
Leendertse P.C., 1105
Leest J., 869
Lerner D., 919
Levacher D., 1135, 1181
Lexmond Th.M., 1201
Libelo E.L., 95
Licarta J., 727
Liesivuori J., 1089
Ligorati R., 949, 1033
Linton J.D., 919
Loch J.P.G., 857
Loibner A.P., 797
Lopez A.G., 163
Lowe M., 1153, 1227
Lubitz B., 1091
Lubrano L., 975, 977
Lukasik K., 1167
Lund W., 897

Lüth J.-C., 531, 1091
Lutz E.J., 143, 571
MacDougall K.A., 943
MacIntyre W.G., 95
Mahro B., 821
Maier N.A., 453
Major D.W., 143, 727, 1187
Mäkelä E., 1089
Malina G., 989
Mangold S., 847
Maniez D., 837
Marker A., 163
Marot F., 1181
Martin I., 729, 1153
Martín I., 1263
Martínez-Sánchez J., 963, 965
Martius G.G.M., 113
Mason J.R., 835, 839, 935
Matsushita T., 1107
Maxin C., 435
McGrath S.P., 123
McLaughlin M.J., 453
McLeod C., 1205
Meharg A.A., 923
Meier-Löhr M., 863
Meiers D.T., 727
Mensch M., 911
Metzger R., 955
Meyer S., 871, 905
Middeldorp P.F., 857
Miethe D., 893
Mikheikin S.V., 1175
Milani A., 691
Mischgofsky F.H.M., 631
Modolo R., 1019
Mol G., 987
Mol S.N., 865
Molnár M., 1051, 1207
Moncaster S., 1035
Montuori V., 691
Morel J.L., 609
Morgan P., 143, 571, 1187
Morris R.S., 917
Mosbæk H., 819
Moser L.E., 1187
Moser R., 905
Mroueh U.-M., 1089, 1129
Muguruza I., 1263
Mulder H., 133
Mulleneers H.A.E., 1075
Müller S., 599, 997, 1177
Munch S.K., 819
Mundó B., 1221
Munz C., 173, 1067, 1253
Murphy J., 661
Nagy G., 1125
Nahold M., 869
Nardella A., 1059
Nasserzadeh V., 1205
Nathanail C.P., 801, 1013
Nathanail J., 1213
Nathanail P., 1213
Neef A., 905
Neef U., 1057
Neeße Th., 877, 879
Neilson R., 883
Němeček J., 961
Neumann H., 1041
NICOLE, 25
Niebelschütz H., 1189
Nielsen S.T., 1141
Nijboer M.H., 1173
Nobili F., 1185
Nordlohne L., 981
Norris G., 413, 1079, 1097
Nortcliff S., 83
Notenboom J., 781
Nouwen J., 757, 993
Nowak B., 1167
Nyholm N., 1001
Nylund K., 261
Oakes D., 1117
O'Brien A.S., 1029
Odam J.M., 143
Ødegård K., 897
Odom J.M. Lee M.D., 571
Oesterholt F.I.H.M., 1073
Okx J.P., 1173
Ólafsdóttir K., 261
Olijve M., 251
Olin M., 1089
Ondruschka B., 599, 997
Oosterbaan J., 213
Oppenheimer M., 1201

O'Riordan N.J., 1019
Ortiz R., 1263
Oste L.A., 1201
Otten A., 191
Ottosen L.M., 471
Paetz A., 83
Pak G.A., 1105
Pandard P., 959
Panin A.V., 867
Papassiopi N., 461
Pardieck D.L., 571
Paterson J.E., 927
Paton G.I., 123
Pazdej R., 825
Peasley B.J., 995
Pegoev A.N., 973
Peltola R., 1197
Pensaert S., 1195
Pepels A.H.M., 1099
Pérez-Sirvent C., 963, 965
Perry J., 765
Persin F., 1161
Peters B., 813
Petruzzelli G., 975, 977, 1139
Pettersen B., 471
Petzold E., 885, 887, 1183
Pezzarossa B., 1139
Phear A., 1019
Philipp R., 1253
Philippe G., 933
Pickard J.A., 841
Pijls C., 1083
Pitea D., 949, 951, 1033
Plant S.J., 413
Plimmer B., 1035
Pluim M.P., 1073
Plunkett J.S., 1027
Podlešáková E., 961
Poinsot-Balaguer N., 1043
Pollard S.J.T., 33, 721, 775, 795, 927
Pörschmann J., 113
Posthuma L., 337
Preston S., 123
Prince M.J., 1087
Prohaska J.A., 539
Pronina L.V., 1175
Przyborowski S., 749
Ptak T., 815
Puhakka J., 1273
Pulford I., 1119
Pulford I.D., 1145, 1225
Puolanne J., 1273
Puri G., 1
Pyy O., 1273
Quandt C., 531
Quint M., 775
Quist J.J., 251
Ramsey M.H., 221, 861
Rees R.M., 927
Rees S., 1225
Reid B.J., 889
Reid J.M., 765
Reimers Ch., 833
Reisinger H.J., 403
Reißfelder M., 957, 1163
Reitz T., 957
Rekolainen S., 1113
Remmler M., 599, 997
Reppe S., 1241
Ridal J.P., 1219
Riddell-Black D., 1145
Rigby C., 1203
Riis V., 893
Rijnaarts H.H.M., 109
Ringeling R.H.P., 907
Ringstad O., 261
Risoul V., 719
Ritz K., 883
Rius J., 1221
Robra K.-H., 1103
Rogers M., 1035
Roland U., 599, 997
Romantschuk M., 1197
Roovers C., 191
Roper M., 1097
Rouse J., 661
Ruardi P.A., 745
Rügge K., 101
Rulkens W.H., 133, 789, 999, 1075
Rüpke A., 651
Rustad I., 261
Rutgers M., 337, 781
Sagarduy M., 1151
Sagarduy R., 1263

Salami I.R.S., 983
Salas O., 1149, 1151
Salkinoja-Salonen M., 1197
Salt C.A., 1113, 1223
Salter R., 1227
Salvo J.J., 143, 727
San Jorge R., 1263
San Martín J., 1263
San Vicente A.I., 1149, 1151
Sandeaux J., 1161
Sandeaux R., 1161
Sanden J., 43, 1243
Sangenstedt Ch., 749
Santos Oliveira J.M., 937
Satijn B., 377
Sauvalle B., 743
Sawata S., 549
Sayles G.D., 727, 1187
Schäfer J., 773
Scheidemann P., 939
Schiedek T., 881
Schies U., 751, 1015
Schlegel T., 523
Schlegl M., 797
Schmid B., 173, 1067
Schmidt M.W.I., 953
Schmidt R., 575
Schneider M., 1103
Schneider R., 773
Schoeters G., 1109
Scholz J., 1177
Scholz R.W., 1191
Schoone M., 953
Schricker B., 877
Schröder T.J., 1201
Schulin R., 1111
Schurink E., 631
Schwartz C., 609
Schwarz R., 815
Schwarzenbach R.C., 1191
Schwedes J., 1177
Seelig-Braker A., 1211
Semmoud A., 837
Semple K.T., 889
Sens C., 939
Seppänen A., 1273
Seuntjens P., 993
Shaw E., 923
Shen C.F., 513
Shimizu Y., 1095
Shirai J., 1037, 1049
Siebert J., 809
Silla M., 981
Sims P., 1165
Sinke A., 109
Siobowicz G., 1167
Sisto R., 1059
Skoufadis C., 461
Skovgaard I.M., 731
Skovgard I.-M., 733
Slenders H., 377, 829, 1063
Smart M.K., 453
Smirnov A.Yu., 1175
Smit A.L., 989
Smit P.J., 725, 1045
Smith M.A., 9
Smith M.V., 1127
Smith P., 331
Smith S., 1117
Sobisch T., 1189
Sobral L., 1133
Soga K., 807
Sokollek V., 1211
Solberg H., 261
Soltysiak G., 1167
Somitsch W., 1103
Sousa S., 839
Spivack J.L., 571
Squire S., 221, 861
Stahl U., 905
Stapleton R., 95
Staps J.J.M., 811
Stäubli B., 1191
Stauffer T.B., 95
Steeds J.E., 425
Steffens K., 809
Stegmann R., 531, 1091, 1131
Steinhart H., 871
Steirer T., 1215
Sterckeman T., 837
Stichnothe H., 1093
Stottmeister U., 113
Struppe H.G., 997
Stubenrauch St., 301

Stukin E.D., 973
Sueyoshi M., 1095
Susaeta I., 1149, 1151
Sutherland W., 761
Sweegers B.M.C., 337
Swithenbank J., 1205
Syms P.M., 671
Syratt W.J., 1289
Szabó P., 1125
Szakács T., 1051
Szelinski B.-A., 1237
Szolar O., 797
Szönyi M., 1207
Szoyka S., 203
Takano Y., 1095
Tambouris S., 461
Tarnowski F., 585
Taylor M.L., 539
Tedd P., 641, 1065
Teutsch G., 815
Theile P., 413
Theißen H., 1015
Theodoratos P., 1115
Thiboutot S., 513
Thimm A., 1183
Thomas A.G., 907
Thomas A.O., 181, 1023, 1097
Thomassen P.H.G., 251
Thöming J., 1093, 1123, 1133
Thybaud E., 959
Tonnaer H., 191
Tramm H., 885, 887
Travesa F., 1221
Trivedi D., 929
Trouvé G., 719
Truffaut N., 933, 959
Tucker P., 801
Tuomainen J., 1273
Turpeinen R., 1197
Turrell J., 845, 1185
Tütem E., 1179
Tye A., 123
Underhill S., 203
Vacca M., 691
Vahanne P., 1089
Vallat Ph., 1253
Valledy B., 775
van Aalst-van Leeuwen M.A., 109, 197
van Alphen M., 857
van Buyzen H, 109
van den Heuvel R., 1109
van der Kammer F., 279
van Drunen M.A., 1173
van Dyck E., 767
van Gaans P.F.M., 987
van Hasselt J., 823
van Heiningen E., 109, 197
van Leeuwen J.L.M., 1099
van Liere H.C., 109
van Sandick O., 1227
van Sandick O.Z., 745
van Straalen N.M., 1025
van Veen R.P.M., 337
van Velsen A.F.M., 251
van Vossen W.J., 829, 1063
van Wensem J., 445
van Zutphen M., 561
Vana J., 1155
Vandecasteele J.P., 791
Vartiainen T., 915
Védrine H., 827
Vegter J.J., 291, 445
Veltrup D., 885
Venghaus T., 479
Verheyen R.F., 993
Vermeij E.J., 777
Verschaeve L., 1109
Vidal J., 963
Viktorov A.G., 1047
Villumsen A., 471
Vinogradoff S.I., 931
Visser W., 729, 731
Vogel C.M., 727, 1187
Vogel T.M., 523
Vogt T., 705
Volkering F., 251
Volkwein S., 367, 1069
von Steiger B., 1111
Vriend S.P., 987
Wahlström M., 1089
Walker R.H. Graham M.C., 929
Wallace S., 65, 1065
Watkinson R.J., 919
Wavrer Ph., 827

Wawrukiewicz A., 1049
Weidemann R., 957, 1163
Weiland-Wascher A., 809
Weinberg R., 981
Weingran C., 393
Weißbrodt E., 113
Weitz H., 839
Weltens R., 1109
Welter E., 847
Wenger C., 1253
Wenger K., 1085
Werner D., 939, 1041
Werner P., 791, 863
Werther J., 479
West R.J., 143
Wetzel A., 1041
Wevers H.H.A.G., 1101
Wheater H., 1117
Wheatley R.E., 883
Wheeler C., 1119
Whittaker M., 795
Wichtery K., 749
Wienberg R., 821
Wießner A., 113
Wilke B.-M., 345
Wille E., 767
Willershausen H., 435
Wilson P., 765
Wind B.S., 337
Winkel B., 345
Wit H. de, 377
Wittmann U., 1245
Woodland S., 383
Woodworth R., 727
Wright P.D., 1229
Young S., 123
Yousfi I., 1021
Zárate G., 1263
Zhang H., 123
Zmirou D., 1005
Zoumis T., 941
Zubiaga R., 1143