Contaminated Soil '98

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

Volume 1

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

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ISBN: 0 7277 2675 7

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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

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Foreword

Looking back at the series of five preceeding conferences, ConSoil is a well established qualified international forum for those engaged in the field of contaminated land:

- scientists exchange the latest results of fundamental research
- engineers present progress in technical innovation
- managers communicate about current and future technologies and business, challenges for prevention of soil contamination and for remediation of polluted sites
- policy makers discuss the shaping of national and international strategies and attempts to harmonize international legislation
- investors, administrators, banking and insurance companies present and exchange news, knowledge and practices.

Encouraged by the wide interest in the fifth conference in Maastricht, the organizers decided to continue the ConSoil series. In preparing the sixth conference, the general scope of the conference programme was retained but additional items were included, such as risk management and technology transfer and the legal, financial and insurance aspects of contaminated land and its utilization. The number of oral presentations has been reduced in favour of extending the time available for case studies and workshops. Company and country presentations, technical tours and a technical exhibition again round up the conference programme. The proceedings have proven to be a valuable documentation of the conference events.

The decision to go to Edinburgh was strongly influenced by the substantial increase of interest in the United Kingdom for our subjects since the early 1990s. Great efforts were made by regional authorities and scientists to hold ConSoil '98 in Scotland. In particular, Scottish Enterprise offered very generous support. The city of Edinburgh and others joined them cordially. Consequently, Scottish Enterprise was appointed the third organizing institution of the 1998 conference. Another important aspect in favour of the Edinburgh venue was the possible combination of ConSoil '98 and the simultaneously occurring event of Urban World '98 in the nearby city of Glasgow.

Once again, the conference is sponsored by generous grants from Germany and the Netherlands, supplemented by support from national and regional governments of Finland, Spain (the Basque Region) and Switzerland.

The response to the call for papers was very good, with more than 500 abstracts for presentations received, from which the Scientific Committee, supported by the Scientific Advisory Board, selected the contributions to a comprehensive programme of lectures, poster presentations and workshops.

We are delighted to welcome many old friends to ConSoil '98 in Edinburgh and look forward to meeting new ones. We are confident that the conference programme, the venue and the social programme will trigger the exchange of valuable information and the establishment of enhanced cooperation.

Prof. Dr Wim Harder
Chairman of the Scientific Committee, TNO

Friedrich Arendt
Chairman of the Organizing Committee, FZK

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SOILS AND SUSTAINABILITY - A NATURAL HERITAGE PERSPECTIVE

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Key words: Soil protection, remediation, sustainable soil use

SUMMARY

Soil is an integral part of our natural heritage in Scotland, as well as an important economic resource. Pressures on soils have intensified from a variety of land use practices and from contamination, raising concerns about the sustainable use of the resource and the possible impacts both on soil functions and on soil biodiversity. This paper first outlines the role and contribution of SNH in facilitating the development of a strategy for soil sustainability in Scotland, an approach now reflected by Government recognising of the need for a national soil protection strategy in Britain. It then addresses the issue of soil contamination in Scotland within the context of such a strategy. A holistic approach which considers all sources of contamination and which views sustainability over the long term will be required, in addition to finding novel ways of remediating sites and using waste materials. New approaches and partnerships will also be required between industry, local authorities, the academic community and government agencies to address remediation and land regeneration.

Contaminated Soil '98, Thomas Telford, London. 1998, 1–5

Soil is the biochemically weathered surface of the Earth and is distinct from sediment as it contains a biological component making it capable of supporting higher plants. It is the interface between lithosphere, atmosphere and biosphere, which gives it unique and complex properties. Soil means different things to different people: to the farmer it is a medium for plant growth, to the engineer it is a surface deposit with mechanical properties, to the industrialist it is a source of minerals and materials, and to the biologist it is an important pool of genetic diversity. In our lifetimes soil is a non-renewable resource which takes hundreds and sometimes thousands of years to develop. Soil maintains habitats and biodiversity and is an integral part of our natural heritage.

SNH's role is to safeguard and enhance the conservation of the natural heritage of Scotland and to foster understanding and enjoyment of the natural heritage. The fundamental principle underlying the work of SNH is that anything done in relation to the natural heritage is done in a manner which is sustainable. From a natural heritage perspective, therefore, SNH has a clear duty to ensure the sustainable management of Scotland's soils. Since the 1940s, pressures on soils in Scotland, as elsewhere in Europe, have increased through intensification of agricultural production, afforestation, disposal of industrial waste and urban expansion. With this has come the recognition, for example in the European Soil Charter, that the soil is a limited natural resource which is easily damaged and requires protection from erosion, pollution and degradation arising from these activities.

Currently, however, there is no legislation in Scotland (or Britain) relating to soil protection, although there are guidelines for farmers set out in a Code of Good Practice (SOAFD, 1992). Against this background, SNH convened a working group in 1992/93 to examine the issues relating to soil protection in Scotland (Gordon, 1994). This led to SNH adopting a facilitative role in the development of a soil sustainability strategy for Scotland to ensure the wise use and management of soils as part of our natural heritage.

As part of this role, SNH held a conference in 1995 on the sustainable use of soils which addressed the pressures on the resource and how these could be reconciled with soil sustainability. One of the main recommendations from that conference was for a multidisciplinary approach to management of the soil, leading to the development of a strategy for soil sustainability in Scotland (Taylor *et al.*, 1996). The key elements of this approach involved:

- identification of opportunities within the existing policy and legislative frameworks for the implementation of solutions or co-ordinated approaches to particular problems;
- agreement of a common research agenda to underpin sustainable soil management;
- identification of how a wider forum on soil sustainability might be established to include land users, land owners and land managers;
- facilitation of the development of a monitoring system to allow early detection of adverse soil changes; and
- evaluation of progress and consideration of the requirements for longer-term action related to soils and sustainability.

In a parallel development, SNH co-ordinated the presentation of evidence from the three country conservation agencies (Countryside Council for Wales, English Nature and SNH) and the Joint Nature Conservation Committee to the Royal Commission on Environmental Pollution (RCEP) study on *Sustainable Use of Soil*. This evidence addressed a number of major issues concerning agricultural use of soils, soil contamination, acidification, climate change, erosion, forestry, soil biota, peat soils, soil monitoring and the need for a co-ordinated national approach to sustainable soil management (Taylor, 1995). In their report to Government the RCEP made a number of recommendations, the most significant of which was that a soil protection policy should be drawn up and implemented for the UK (RCEP, 1996). This would be in line with soil protection concepts and policies already in place in Europe (*e.g.* German Soil Protection Concept, 1985; Netherlands Soil Protection Act, 1987). Government responded favourably to the RCEP report and has indicated that a national strategy for soil protection should be formulated (DoE, 1997). SNH is therefore well placed to contribute to this process.

Soil contamination is one important issue identified by SNH for action within a national strategy for soil protection. Particularly in central Scotland, there is a legacy of contamination from point sources which needs to be addressed if soils are to perform their full range of functions. A large proportion of our contaminated land is a historical legacy from past industrial practice associated with coal and metaliferrous mining, industrial processes and urban waste. New approaches and partnerships will be required between industry, local authorities, the academic community and government agencies to address remediation and land regeneration. There is a challenge to find new ways of remediation, which in the past have involved rather drastic measures such as soil removal or burial prior to re-use. However, new techniques now hold out the prospect of improving soils *in situ* using biological methods. It will be important to develop these methods of bio-remediation further, to ensure that they are both economically viable and environmentally acceptable and to apply them in practice to return contaminated land to productive use or to restore its natural heritage value. The re-use of 'brownfield' sites for appropriate purposes will also form an important element of a national soil protection strategy.

In Scotland, soil contamination has also arisen from diffuse pollution, the sources being burning of fossil fuels, which releases trace metals and oxides of sulphur and nitrogen, and aerially dispersed acids and metals from industrial processes. In addition, incidents such as Chernobyl have resulted in deposition of a significant quantity of radionucleides, particularly in semi-natural upland areas. While international agreements are now in place to reduce the quantity of pollutants being emitted, we also need to understand how the contaminants are affecting soil properties and functions and to monitor any changes in soil condition. Scottish soils, in particular, are vulnerable to accelerated acidification by virtue of their intrinsic properties, which in turn makes trace or heavy metals more mobile within the soil. We need to assess what loads of contaminants different soils are capable of absorbing before soil functions are lost and contaminants begin to be released into the wider environment. We also need to consider how we can use waste materials and by-products of industrial processes as soil forming materials and how we can reduce the

loss of topsoil from urban and industrial developments. This requires a deeper understanding of soil forming processes and how we can best protect displaced soil. It also requires co-operation between industry, soil users, the academic community, local authorities and government agencies to ensure the best possible use of soil.

In the lowland agricultural areas there have been problems of contamination by agrochemicals, nutrient leaching and disposal of farm waste. Many of these problems are being addressed, for example through codes of practice. The challenge is to ensure communication of the benefits of adopting such practices and to foster 'ownership' among land users. The adoption of management practices specifically, rather than incidentally, to benefit nature conservation should also be encouraged where appropriate.

Looking to the near future, there will be additional pressures on our soils through the disposal of sewage sludge as dumping at sea is phased out. We need to be able predict the effects this will have on soils and how we can reduce any potentially adverse impacts on soil functions and on soil biota.

Monitoring the state of quality of the soil, as reflected in appropriate indicators, as well as the effectiveness of remediation of contaminated soils over the long term, will be an integral component of a national soil protection strategy, and it is appropriate that bodies such as SNH are involved. Given the scale and potential costs of cleaning up and protecting our soil resource from further degradation, environmental agencies will need to work in partnership with land users, since it is in the interests of all parties to preserve and enhance soil functions and properties to leave the soil with the potential for the maximum number of possible uses.

In conclusion, soil is a vital part of our ecosystems. It behaves as a buffer, filter, store and biological reactor in addition to sustaining agricultural productivity. There are real limits to the load of contaminants which the soil can contain. We need to ensure there is a balance between the soil's capacity to receive contamination and the economic costs to society of remediation and altering industrial/agricultural practice. This can be achieved through partnership between the users of soil resources and the agencies responsible for its protection. As far as possible, opportunities within existing policy and legislative frameworks should be explored for the implementation of solutions or co-ordinated approaches to particular problems. A holistic approach which considers all sources of contamination and which views sustainability over the long term is required, in addition to finding novel ways of remediating sites and using waste materials. In the future, soils will become more important as a sink for waste material and we must ensure that long-term damage to soil properties and functions is avoided in an economically acceptable manner.

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CONTAMINATED SOIL '98

Theme A:
International cooperation

COMPARATIVE INTERNATIONAL STUDY OF SOIL AND GROUNDWATER REMEDIATION TECHNOLOGIES

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Key words: case study, clean-up technologies, decontamination techniques, government, in-situ treatment, knowledge transfer, off-site treatment, on-site treatments, remediation, remediation efficiency.

SUMMARY

The final technical report of the NATO Committee on the Challenges of Modern Society (NATO/CCMS) Pilot Study on the *Evaluation of Demonstrated and Emerging Technologies for Treatment and Clean-up of Contaminated Land and for Groundwater* will be published during 1998. The Pilot Study provided information and technology exchange between twenty four countries through critical review of over 50 projects, and themed discussions at the meetings of the Study Group.

KURZFASSUNG

Der technische Abschlußbericht der Pilotstudie *Evaluation of Demonstrated and Emerging Technologies for Treatment and Clean-up of Contaminated Land and for Groundwater* des NATO Committee on the Challenges of Modern Society (NATO/CCMS) wird im Laufe des Jahres 1998 veröffentlicht. In der Pilotstudie fand ein Informationsaustausch zum Technologietransfer zwischen Vertretern aus vierundzwanzig Nationen statt, dazu wurden mehr als 50 Projekte kritisch untersucht und diskutiert.

RÉSUMÉ

Le rapport technique final du Comité OTAN sur les Chalenges de la Société Moderne intitule "*Etude pilote d'évaluation de techniques innovantes ou expérimentales sur le traitement et las réhabilitation de sites contaminés et d'eaux souterraines*" sera publié dans le courant de l'année 1988. Cette étude pilote founit d'une part des informations et une étude comparative de technologies issues de vingt - quatre pays au travers d'un examen critique de plu cinquante projects et d'autre part les discussions thématiques des réunions du groupe d'étude.

Contaminated Soil '98, Thomas Telford, London, 1998, 9–18

1. INTRODUCTION

The final report[1] of the NATO Committee on the Challenges of Modern Society (NATO/CCMS) Pilot Study on the *Evaluation of Demonstrated and Emerging Technologies for Treatment and Clean-up of Contaminated Land and for Groundwater* will be published during 1998. Over fifty projects, ranging in scale from bench studies through to full-scale remediation projects were critically reviewed during the study to identify "lessons learned", not only from fully successful projects, but also from those which illustrated technology failures or limitations. Attention was paid not only to the technologies themselves, but also to the practical, operational and organisational aspects.

NATO/CCMS has sponsored a number of earlier Pilot Studies on the technical aspects of contaminated land. The first CCMS study on contaminated land[2] (1980-1984) comprised a desk study of available remediation methods. This led to a the "Phase I" study[3] (1986-1991) to identify and evaluate innovative, emerging and alternative technologies and to transfer technical performance and economic information on them to potential users.

The final report[1] of the recently completed Phase II study provides: information on the background and organisation of the Pilot Study; a short description of each of the more than 50 projects included in the study; characterisation of the projects in a variety of ways including, for example, by their development status (e.g. emerging or demonstration), technologies used, and contaminants treated; a critical review of the results of each of the projects in a series of technology based chapters, and the conclusions and recommendations arising from the Pilot Study. A description the organisation of Pilot Study, and a summary of its achievements, key conclusions and the recommendations to the Committee on the Challenges of Modern Society has been published in a separate Overview Report[4].

The study was conducted under the joint leadership of the United States, the Federal Republic of Germany, and the Netherlands. It was co-chaired by Mr Stephen James and Dr Walter Kovalick Jnr. of the United States Environmental Protection Agency (the "Pilot Study Directors"). Australia, Austria, Canada, the Czech Republic, Denmark, France, Germany, Hungary, the Netherlands, Norway, Sweden, Switzerland, Turkey, the United Kingdom and the United States provided projects to the study. In addition, Belgium, Hong Kong, Italy, New Zealand, Poland, Portugal, Romania, Slovenia and the Slovak Republic were represented at one or more meetings by a government representative, a CCMS Fellow or an individual expert.

The objectives were to: exchange technical information on demonstrated technologies, exchange information on the development of new technologies, and recommend, develop and adopt uniform data reporting methods for results from technology studies (demonstrations, bench, pilot and other technology studies). The last objective was intended to make it easier for others to evaluate the probable performance of a technology based on the particular environmental or health/risk standards of that country. The need for better reporting standards was identified during the Phase I

study. However, the nascent stage of technical developments in many countries did not permit this objective to be fully addressed. It is anticipated that it will be addressed further during the Phase III study (see Section 6 below).

The Pilot Study Group held seven meetings at which countries submitted candidate projects for discussion and voting on for inclusion in the study. In-depth interim and final project report presentations on the conduct and results of these projects were made during the meetings. Written reports were published in the proceedings of each meeting. Each meeting also included host country presentations plus a "tour de table' during which each member country described developments in its national legislation, regulations and research and development programmes. In addition, recognised experts in diverse technical fields gave invited papers related to the challenges in soil and groundwater remediation and NATO/CCMS Fellows provided presentations and written reports on their work.

2. RELATIONSHIP WITH OTHER CCMS PROGRAMMES

The CCMS awards Fellowships each year to meet travel and subsistence costs for projects related to on-going Pilot Studies. Fellows are encouraged to attend meetings of the Study Groups. CCMS Fellows made an important contribution to the success of this Pilot Study, as it did to the two earlier Pilot Studies on the remediation of contaminated land. The award of fellowships enabled the participation of a number of individual experts including from countries which would not otherwise have had a presence in the Pilot Study and enabled a wider range of topics to be covered than would otherwise have been possible. In addition, participation of a number of individuals, particularly expert speakers, was made possible by travel funds provided under the CCMS Study Visit Programme.

Ten NATO Fellows were associated with the Pilot Study: nine conducted associated studies and submitted reports to the Pilot Study, one edited the final report and two contributed to its preparation. The Fellows came from private, university and governmental organisations in Germany, Portugal, The Netherlands, the United Kingdom and the United States. Their activities covered a range of topics including an examination of the national approach to such problems, costs and economics, quality management, innovative approaches to large scale remediation projects, and assessment of the performance of in-situ treatment methods. Summary reports provided by Fellows are to be published as Appendix V (Volume 3) of the Final Report.

3. ACCOMPLISHMENTS

The Pilot Study Group examined 52 remediation technology projects from fourteen countries over the five year course of the study. The projects encompassed in-situ and ex-situ biological, chemical/ physical and thermal treatment technologies. Many of the projects involved two or more technologies, either in integrated treatment systems or in parallel treatment of different contamination problems.

Non-member countries, including a number of NATO Cooperation Partner countries took increasing interest in, and advantage of, the Phase II Pilot Study. For example: (a) the first international meeting was held in Budapest in 1992 - the first CCMS meeting to be held in a Cooperation Partner country; (b) an international conference was held in Adelaide, Australia in 1995; (c) projects were contributed to the study by a number of non-member countries including Australia, the Czech Republic, Hungary, Sweden and Switzerland.

The study was designed to provide governments with a broader view of the research strategies of other countries in order to help them focus their own research strategy. For example, the German Federal Ministry of Environment, Nature Protection and Reactor Safety commissioned one of the Fellows to prepare a report[5] of the meeting held in Berlin in 1996 and a review of research needs.

Close liaison was maintained throughout the study with other international groups dealing with the problems of contaminated land including: (a) the CCMS Pilot Study on the Environmental Aspects of Reusing Military Lands; (b) the "Ad-hoc International Working Group" on Contaminated Land; (c) the Common Forum on Contaminated Land in the European Union; (d) CARACAS (the European Unions's Concerted Action on Risk Assessment for Contaminated Sites); (e) NICOLE (the European Union's Concerted Action - Network for Industrially Contaminated Land in Europe); (f) the International Organisation for Standardisation's (ISO) Technical Committee TC 190: Soil Quality; and (g) the German-United States Bilateral Agreement, the goals of which are to facilitate an understanding of each country's approach to the remediation of contaminated sites, demonstrate innovative remedial technologies, compare quality assurance programmes, and facilitate technology transfer.

4. TECHNICAL OVERVIEW

There were fifty two "active" projects in the study (see Table 2). A number of the projects were in practice only phases in longer studies. In addition, some projects were delayed and have been carried forward to the Phase III study. Where appropriate these projects have been included in the analyses presented below. A large proportion of the projects involved more than one technology - some involved the use of integrated treatment systems combining more than one technology type and others involved the application of more than one technology to deal with separate aspects of contamination of a site (e.g. groundwater vs soil). Other projects concerned: large scale remediation projects for which the remediation strategy had yet to be developed, theoretical studies and strategic scientific studies. The projects are classified below in a variety of ways. It should be noted that: in some of the analyses projects may be double or treble counted, not all projects are included in each analysis, and the categorisation of projects is in part at a matter of judgment - alternative categorisations to those presented here are possible.

Forty nine of the fifty two projects were technology based. The Pilot Study accepted technical projects in two areas of development: **emerging** and **demonstration**. For the

purposes of the study an emerging technology was defined as being at bench- or pilot-scale whilst a demonstrated technology was one implemented at field- or full-scale. Demonstrated technologies were usually at or near to commercial application. There was almost a fifty-fifty split of projects within the Pilot Study examining emerging and demonstrated technologies. Eighteen of the projects were classified as in-situ, 26 as ex-situ, and 6 as combining in-situ and ex-situ treatment.

For the purposes of the study the technologies described in each technical project were broadly classified as one of five types: **biological**, **chemical**, **physico-chemical**, **stabilisation/solidification**, and **thermal** - see Table 1.

Table 1: Categorisation of projects by technologies employed

Technology	Number of Projects	Examples of technologies etc.
biological	24	bioventing, biopiles, slurry reactors, white rot fungi
physico-chemical	29	soil vapour extraction, soil washing, solvent extraction
chemical	4	oxidation with ozone
thermal	5	-
stabilisation/solidification	2	-
other	4	-

The additional categories of **integrated** and **mixed** were used to describe combinations of technologies used as part of an overall remediation strategy. **Integrated** refers to approaches involving process integration where two or more technologies are used simultaneously or in series to treat a specific site problem. **Mixed** projects involved two or more technologies used to treat different contaminated areas or media across a site as part of an overall remedial strategy. The breakdown by use of single, integrated or mixed technologies was as follows: single technology 23, integrated 19, mixed 7, other 3. Typical combinations were soil vapour extraction with in-situ biotreatment, soil washing followed by biotreatment, and soil washing followed by thermal treatment.

Most of the projects (40) were concerned only with the treatment of organic contaminants including PAHs, PCBs, and BTEX compounds. Only six projects dealt exclusively with metals whilst a similar number dealt with a mixture of inorganic and organic contaminants. One project focused on remediation of inorganic sulphates and cyanides.

5. CONCLUSIONS OF THE STUDY

This second technology evaluation Pilot Study again demonstrated the benefits of exchanging technical and economic information on contaminated land and groundwater remediation technologies. The full conclusions of the Pilot Study are presented in the Final Report together with supporting statements. A number of the conclusions listed in the Final Report regarded as of particular importance and drawn to the attention of CCMS as follows:

(a) In a number of countries, remediation strategies are moving from technology-intensive treatment processes to greater recognition of land use management and extensive approaches such as natural attenuation. Further research into these approaches is needed.

(b) The intended future use of a site is increasingly a determining factor when setting clean-up objectives and selecting a remediation strategy.

(c) All remediation activities require proper operation and management.

(d) Whenever possible, the wider environmental impacts of a chosen remedial strategy should be considered during remedial selection.

(e) Integrated treatment systems are frequently needed for site remediation.

(f) Energy efficiency practices influence plant design resulting in varying processing costs between countries. This may make cost comparisons between countries difficult and lead to the choice of different technologies to address similar problems.

(g) Independent evaluation and verification of technologies, and uniform data collection are needed for effective technology transfer.

(h) Scientific understanding of processes is essential to avoid forming harmful end- or by-products, ensure process optimisation, avoid unwanted transfer of contaminants to other media, and understand the limits of technical performance.

(i) Field-scale studies aimed at understanding phenomena such as transport of contaminants and natural attenuation are needed. International collaboration on this effort would increase the value and diversity of conditions studied and lead to quicker application of results.

(d) Although treatment and permanent solutions are widely sought, some contamination problems occur on a scale and complexity for which containment may be the preferred technical and economically viable solution. Further information sharing among countries is needed to determine the long-term effectiveness and state of development of containment systems.

6. THE PHASE III PILOT STUDY

The Country Representatives and other participants in the Study discussed the need for, and the possible scope of a Phase III study on a number of occasions. It was agreed that there would be merit in an extended study both for those countries with established programmes to deal with contaminated land and for those who have more recently begun to address the associated problems - such as countries in central and eastern Europe. In addition, there would be benefits for developing countries who might be

helped to avoid the environmental degradation that accompanied the industrialisation of, for example, Europe and North America. Particular needs identified include more extensive, cheaper and sustainable treatment technologies and the inclusion of studies of containment methods. The first meeting of the new Pilot Study was held in Austria in February 1998. For more information on Phase III, contact your country representative.

Table 2: Projects Included in CCMS Study on Remediation Technology

	Table 2
Country	**Title**
Australia	Field trial of air-sparging aimed at remediating a petroleum contaminated aquifer Bioremediation of petrochemicals following a major fire Bioclogging of aquifers for containment and remediation of organic contaminants Remediation of methyl ethyl ketone contaminated soil and groundwater
Austria	In-situ bioremediation, bioavailability and process control under different soil types
Canada	In-situ/on-site bioremediation of wood treatment soils Demonstration testing of thermal gas phase reduction process Biodegradation/bioventing of oil contaminated soils Field demonstration of an in-situ process for soil remediation using well points Integrated treatment technology for the recovery of inorganic and organic contaminants in soil
Czech Republic	Wood treatment plant, Sobéslav, South Bohemia Spolchemie a.s. - Mercury contaminated site
Denmark	On-site biological degradation of PAHs in soil at former gas works sites Groundwater and soil remediation at former manganese sulphate production plant Thermal treatment at Valby gasworks site
France	Ozone treatment of contaminated groundwater Combined chemical and microbiological treatment of coking sites (complex contamination) Combined vacuum extraction and in-situ stripping of chlorinated organics Solvent extraction/washing Bioremediation of soils from coal and petroleum tar distillation plants

	Table 2
Germany	Biological in situ remediation of contaminated gas works sites Cleaning of mercury contaminated soil by using a combined washing and distillation process Fluidized bed soil cleaning process Mobil low temperature thermal treatment process Permeable treatment beds
Hungary	Environmental evaluation of former Soviet military bases
Netherlands	Modelling and optimisation of in-situ remediation Combined remediation technique for soil containing organic contaminants: combined hydrocyclone separation, photochemical treatment and bioremediation Slurry reactor for soil treatment In-situ bioremediation of chloroethene-contaminated soil
Norway	Treatment of creosote-contaminated soil (soil washing and slurry phase bio-reactors) Soil washing and chemical dehalogenation of PCB-contaminated soil Use of white-rot fungi for bioremediation of creosote-contaminated soil
Sweden	Treatment of PAH and PCP contaminated soil in slurry phase reactors
Switzerland	Long-term biodegradation of hydrocarbons in soils/ reuse of remediated soils
Turkey	Sorption/solidification of selected heavy metals/radionuclides from water on to unconventional sorbents.

	Table 2
United Kingdom	Soil clean-up via separation technology
	Decontamination of metalliferous mining wastes
	"Cacitox" soil treatment technology
	In-pulp decontamination of contaminated sludges and sediments.
	Chemical fixation of soils contaminated with organic chemicals
	Combined in-situ soil vapour extraction within containment cells and subsequent ex-situ bioremediation
	Investigation of enhancement techniques for ex-situ treatment techniques for ex-situ soil separation processes particularly with regard to fine particles
United States	Bioventing of hydrocarbon contaminated soils in the sub-arctic
	Demonstration of Peroxidation Systems Inc Perox-Pure™ advanced chemical oxidation technology for treating groundwater
	Management of soil vapours at the Basket Creek site
	Hand-D contaminant destruction process (groundwater remediation system)
	In-situ microbial filters
	In-situ pneumatic fracturing and biotreatment
	Multi-vendor treatability demonstration of bioremediation technology
	Brodhead Creek in-situ coal tar recovery
	In-situ electro-osmosis (Lasagne project)
	Cooperative approach to application of advanced environmental technologies
	Czechowice oil refinery project

6. ACKNOWLEDGEMENTS

The Final Report of the Pilot Study was prepared by a voluntary writing team drawn from a number of countries. The Pilot Study Directors would like to acknowledge the efforts of the members of the team without whose contributions it would not have been possible to produce the report. Contributions towards the costs of preparing the Final Report were made by Denmark, Germany, Norway, Sweden, the United Kingdom and the United States. The Pilot Study Directors would also like to acknowledge the help given by Dr Deniz Beten of the NATO Scientific and Environmental Affairs Division throughout the study, the authorities and individuals who helped to organise and support the international meetings, and the many individual participants who put time and effort into bringing the study to a successful conclusion.

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CONCERTED ACTION ON RISK ASSESSMENT FOR CONTAMINATED SITES IN THE EUROPEAN UNION - CARACAS

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Key Words: authorities, concerted action, contaminated sites, European Union, knowledge transfer, programme of research, risk analysis, risk assessment.

SUMMARY

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 by their environmental authorities and scientific advisors. The main objective of CARACAS is to co-ordinate current research initiatives on contaminated land risk assessment in Europe and to define priority research tasks for the development of future R&D programmes. The paper describes the results achieved in this project and the expected benefits for the scientific community in Europe.

KURZFASSUNG

CARACAS ist eine konzertierte Aktion im Rahmen des Umwelt- und Klimaprogrammes der Europäischen Kommission DG XII. 16 europäische Länder sind durch nationalen Umweltbehörden und wissenschaftliche Berater in dem Projekt vertreten. Ziel von CARACAS ist die Koordination laufender F&E Initiativen im Bereich der Gefährdungsabschätzung von Altlasten in Europa und die Feststellung prioritärer Forschungsaufgaben für die Erstellung zukünftige F&E Programme. Der Beitrag faßt die erzielten Projektergebnisse zusammen und beschreibt den zu erwartenden Nutzen für europäische Wissenschafter.

Contaminated Soil '98, Thomas Telford, London, 1998, 19–24

INTRODUCTION

The pollution of soil and groundwater from hazardous waste sites and abandoned and existing industrial estates is a complex environmental problem in all industrialised countries. Within the European Union, several Member States have developed or are currently developing frameworks and procedures for assessing and managing the risks posed by contaminated sites. In order to concentrate these efforts and to support harmonised principles for environmental protection legislation within the European Union, a scientific co-operation between European countries has been initiated: the Concerted Action on Risk Assessment for Contaminated Sites - CARACAS.

CARACAS - AN INTERNATIONAL PARTNERSHIP

The Concerted Action CARACAS is carried out by participants from the following countries:

Austria	France	Italy	Spain
Belgium	Germany	Netherlands	Sweden
Denmark	Greece	Norway	Switzerland
Finland	Ireland	Portugal	United Kingdom

Each of these countries is represented by the national Environment Authority and one or two scientific advisors. The project is funded by the European Commission DG XII within the Environment & Climate Programme 1994-98 and co-ordinated by the German Federal Environmental Agency (Umweltbundesamt). CARACAS was launched at the beginning of 1996 and will continue until mid 1998.

PRIMARY OBJECTIVES

The work programme of CARACAS focuses on the co-ordination of research in order to improve scientific knowledge on assessing risks from contaminated sites. The results will help in focusing future R&D programmes and will strengthen the collaboration between European scientists in this environmental field. The primary objectives of CARACAS are:

- identification and compilation of relevant R&D projects for risk assessment of contaminated sites
- summary on risk assessment methodologies in European countries
- evaluation of the practical State-of-the-Art of risk assessment for contaminated sites
- recommendations on scientific priorities for future R&D programmes
- establishment of an information network on risk assessment issues in Europe
- stimulation of multinational co-operation between European scientists
- co-operation with major international initiatives on contaminated land

SCIENTIFIC WORK PROGRAMME

Within the CARACAS project, seven scientific topic groups have been set up to address specific aspects of Contaminated Land Risk Assessment (CLaRA).

Human Toxicology - Topic Group 1 focuses on issues such as appropriateness of primary toxicology data (exposure conditions, mode of delivery, chemical form); extrapolation from high to low doses and from animal to man; mechanisms of toxicity; exposure to mixtures; and bioavailability of contaminants in a soil matrix.

Ecological risk assessment - Topic Group 2 involves characterising exposure and effects in various organisms and biological systems, including issues of bioconcentration, bioaccumulation and biomagnification. There are particular problems in interpreting multispecies exposure to mixtures of components, not all of them known or well characterised.

Fate and Transport of Contaminants - Topic Group 3 is concerned with many issues relevant to removal, attenuation, phase transfer and bioavailability of contaminants, especially in complex mixtures. Processes include speciation, bio- and photodegradation, plant uptake, sorption/desorption, dissolution, diffusion and volatilisation.

Site Investigation/Analysis - Topic Group 4 is concerned with reviewing national approaches to sampling and analysis, and identifying the most crucial parameters for risk assessment. It will seek to make recommendations on data quality needs and good scientific practice to ensure appropriate statistically valid, and cost effective data.

Models - Topic Group 5 reviews the models available in the CLaRA community, including priority setting models and exposure/risk assessment models. Models will be classified according to purpose of application, targets of concern, scientific basis and use status. An important area will be to improve the validation and applicability of models.

Screening/Guideline Values - The role of screening/guideline values, and the scientific and policy basis for them, will be addressed by Topic Group 6. The Group will compare and contrast different soil policy approaches, and the role of guideline values in soil management frameworks. Various protocols for deriving these values will be examined including basic assumptions and methodological aspects.

Methods for Risk Assessment - A seventh Topic Group is charged with reviewing and making recommendations on methods to integrate the basic elements of risk assessment such as soil, sediment and groundwater sampling, exposure modelling and measurement, effects assessment and risk evaluation.

PROJECT RESULTS

Results of the CARACAS project have been compiled in the following works, which are available for all interested parties:

Report "Risk Assessment Methodologies for Contaminated Sites in Europe"
CARACAS delegations provided up-to-date information on their national risk assessment approaches and related scientific concerns. These *Country Reports* were compiled and issued in the first CARACAS Report in February 1997.

Report "State-of-the-Art of Risk Assessment in Europe"
Project data included in the R&D database, and information provided by CARACAS delegations, have been reviewed and assessed by the CARACAS Topic Groups. Their conclusions have been summarised in *Topic Group Papers*, which have been compiled and issued in the second CARACAS Report in September 1997.

Report "R&D Needs for Improvement of Contaminated Land Risk Assessment"
Based on conclusions reached during the project, CARACAS scientists defined priority needs for future research efforts. These recommendations aim to provide a basis for the development of future R&D Programmes, both on a European and national level, in order to co-ordinate future scientific efforts in this field. These CARACAS R&D Recommendations were issued in January 1998.

CARACAS Final Publication "Risk Assessment of Contaminated Sites in Europe"
Conclusions and recommendations elaborated during the CARACAS project will be summarised in a final publication comprising three volumes. Volume 1 combines the scientific conclusions elaborated in the CARACAS project; Volume 2 summarises the national approaches carried out in European countries; and Volume 3 provides information on international initiatives, and the R&D database disks. This CARACAS publication will be available at the ConSoil Conference.

R&D Database
To support the evaluation of the current State-of-the-Art on contaminated land risk assessment, relevant R&D projects in Europe have been identified through national surveys conducted by CARACAS delegations. R&D project information was reported through returning R&D Questionnaires. All reported project data have been compiled in a R&D Database. Currently, the database covers more than 600 R&D Projects on contaminated land risk assessment. The compiled information includes title, abstract, research area, contacts, references, and stage of each project.

CARACAS products can be downloaded from the CARACAS Website at
http://www.caracas.at

NETWORKING

Information network

One major objective of the CARACAS Project is to establish an information network on contaminated land risk assessment in Europe. Approximately 1.200 scientists world-wide expressed their interest in receiving regular information from the Concerted Action CARACAS. Information transfer was started by setting up a CARACAS Newsletter, and has recently increased by setting up a CARACAS WWW site on Internet (http://www.caracas.at). The CARACAS Website aims to become a major information source on contaminated land risk assessment for scientists in Europe. CARACAS reports are available for download at this site. Additionally, the CARACAS R&D database could be a useful tool allowing individual researchers to establish scientific links with colleagues in other countries. It is planned to include the R&D database in the CARACAS Website soon.

Scientific network

Eight CARACAS Workgroup Meetings have been held in Brussels, Hanover, Stockholm, Nancy, Vienna, Brighton, Bilbao, Nottingham, and Berlin. Based on these meetings, a productive scientific network between CARACAS participants has been established. CARACAS participants are co-operating on key areas of risk assessment in the seven scientific Topic Groups, and are jointly developing research proposals in several areas. For example:

Risk Contribution of Contaminated Sites in Urban Environment (RICOCOS) - The main objective is to quantify the risk contribution of contaminated soil relative to other risk contributors in an urban environment, and to develop a conceptual model for estimating the relative risk contributions.

Development and Validation of a Procedure for Ecological Risk Assessment of Contaminated Soil (ERACS) - The main objectives are to establish an approach for including toxicity, chemical speciation, and bioavailability monitoring in risk assessment systems for contaminated sites; to establish a suite of tests covering the needs; and to establish an approach for including statistical data collection in site-specific studies.

Network of International Initiatives on Contaminated Land

The CARACAS Network has established links with some major international initiatives on contaminated land, such as:

- NICOLE - Network of Industrially Contaminated Land in Europe
- European Environment Agency / Topic Centre Soil
- RACE - Risk Abatement Centre for Central and Eastern Europe
- ISO/TC 190/SC 7 - Soil Quality, Soil and Site Assessment
- Ad Hoc International Working Group on Contaminated Land
- NATO/CCMS Pilot Study programme

Several areas of co-operation have been established with NICOLE, an industry led Network on Contaminated Land which is also supported within the EC Environment & Climate Programme. This co-operation resulted in a joint CARACAS/NICOLE Statement about the need for further research activities on contaminated land and recommendations on priority research areas. This statement can be obtained from the NICOLE Website at http://www.nicole.ici.org.

Furthermore, information exchange has been established with responsible authorities outside Europe, e.g. the US-EPA, Environment Canada, the Health Department and EPA of South Australia, and the Environment Ministry of New Zealand.

PROSPECT

The international co-operation successfully started within the CARACAS project has led to another concerted action between the European Member States. The Concerted Action CLARINET, Contaminated Land Rehabilitation Network for Environmental Technologies, will be launched in mid 1998. The primary objective of CLARINET is to develop technical recommendations for sound decision making for the rehabilitation of contaminated sites based on current scientific knowledge.

Further information

Further information on the Concerted Action CARACAS can be obtained from the CARACAS Website (http://www.caracas.at).

WORKSHOP ON CONCERTED ACTIONS ON CONTAMINATED SITES IN THE EUROPEAN UNION - CARACAS, NICOLE, CLARINET

Key Words: authorities, concerted action, contaminated sites, European Union, knowledge transfer, programme of research, risk assessment, clean-up technologies.

SUMMARY

Two Concerted Action programmes, CARACAS (authority led) and NICOLE (industry led), were established in 1996 as part of the Environment and Climate RTD Programme of the European Commission to tackle the problem of contaminated land. Both networks identified very similar areas which would benefit from further Research and Development initiatives. These recommendations for future research efforts are summarised in this paper. At the ConSoil '98 workshop, CARACAS and NICOLE will present and discuss results and benefits of concerted initiatives. Furthermore, all workshop participants will be informed about the planned Concerted Action CLARINET and are invited to formulate expectations and suggestions for this future network.

KURZFASSUNG

Anfang 1996 wurden zwei konzertierte Aktionen im Rahmen des Umwelt- und Klimaprogrammes der Europäischen Kommission gestartet, - CARACAS (Umweltbehörden) und NICOLE (Industrie). Die beiden Projekte haben in einem gemeinsam verfaßten Informationsblatt Empfehlungen für zukünftige F&E Initiativen veröffentlicht. Diese F&E Empfehlungen sind in diesem Beitrag zusammengefaßt. In einem gemeinsamen ConSoil '98 Workshop werden die erzielten Ergebnisse und Erfahrungen präsentiert, sowie die Vorteile konzertierter Aktionen diskutiert. Darüber hinaus werden die Workshop Teilnehmer eingeladen, ihre Vorschläge und Erwartungen in die neue konzertierte Aktion CLARINET einzubringen.

Contaminated Soil '98, Thomas Telford, London, 1998, 25–30

INTRODUCTION

Past and present human activities which introduce contaminants to the soil and groundwater have resulted in some 750,000 sites across Europe with suspected contamination. Some of these sites may endanger water resources, ecosystems, and/or human health.

Better methods are needed for assessing the likely impacts on humans and the environment:

- to confirm that sites are fit for their current or intended uses
- to guide the remedial actions needed to ensure fitness for use and a reduced burden of aftercare for future generations.

Concerted Action programmes - CARACAS, NICOLE and CLARINET

The Concerted Action programmes, CARACAS and NICOLE, were established in 1996 as part of the Environment and Climate RTD Programme of the European Commission to tackle the problem of contaminated land. They bring together the combined knowledge of academics, government experts, consultants, industrial land owners and technology developers. The two Concerted Actions approached the problem from different perspectives. NICOLE's focus is primarily on industrial sites still in use or owned by industry. CARACAS has the broader perspective of governments who have to make rational decisions within a national contaminated land policy and planning framework. A third Concerted Action CLARINET will be launched in mid 1998. CLARINET will develop technical recommendations for sound decision making for the rehabilitation of contaminated sites.

Towards a Better Future - Establishing Fitness for Use and Sustainable Development of Contaminated Land in Europe

Land is "fit for use" when it can be used for a particular purpose without posing unacceptable risk to human health or the environment. Uncertainties about the nature and significance of chemical contamination can be a major stumbling block hindering sustainable development, and increasing pressures on greenfield sites. Without more cost-effective methods for assessing fitness for use, large sums of government and industry money may be spent on sites that cause little environmental impact, while other sites which are in greater need of attention may not receive it.

There are many areas where significant improvements in the science base would greatly reduce the cost and increase the certainty of fitness-for-use assessments. Both Concerted Actions, CARACAS (authority led) and NICOLE (industry led), identified very similar areas which would benefit from further Research and Development initiatives as described in this joint statement.

Together the two programmes are working to provide a vision, and identify the means, by which risk assessment and management can be applied effectively to ensure the safe use of these lands to protect the environment.

Effective solutions require:

- the close collaboration of scientists and engineers, industry problem holders, policy makers, technology developers, academics, and research programme planners
- focused and transparent approaches that are economically viable.

The results will be important to us all for:

- a safe and attractive environment
- sustainable reuse of former industrial areas for homes, businesses and leisure areas
- effective and timely solutions at a viable cost to society.

Research Needs

Research should provide a variety of decision-making tools for managing and solving contaminated land problems. Decision-making tools can take various forms such as sampling protocols, transport models, tiered risk assessment frameworks and soil screening values. A focused research effort with international co-ordination is needed:

- to provide a high quality base for peer review
- to stimulate co-operation and harmonisation to avoid duplication of research at the national level.

"Fitness for use" focuses on the relationship between soil and groundwater quality and human land use and natural ecosystems. This provides two starting points for research:

- ***The nature of contaminated land:*** the fate, transport, biodegradation and long term behaviour of soil pollutants.
- ***Fitness for use:*** understanding the demands on soil quality and risk acceptability for various form of land use.

The first theme focuses on the soil environment and the second on human health and ecological risks, and the perception of these risks. Risk communication and the economic consequences of soil pollution are also central to the implementation of policies. A third theme is remedial actions. This will lead to a range of feasible short term and long term solutions. A new Concerted Action CLARINET will consider remedial actions in conjunction with decision-making frameworks.

RESEARCH NEEDS

1 The Nature of Contaminated Land

A) Site characterisation: extent, intensity and environmental transport and fate of pollution

- robust and rapid low-cost techniques for investigation of potentially contaminated sites
- improved methods for estimating the accuracy and variability of the whole sampling and analytical process
- methods that yield information at spatial scales relevant for exposure assessment
- characterisation by biosensors and bioassays
- methods to assess migration of groundwater contamination
- methods to assess the natural potential of soil to reduce contaminants to acceptable risk levels and to monitor the process
- the interaction and general fate of contaminant mixtures
- detection of non-aqueous phase liquids and the prediction of their fate.

B) Bioavailability of contaminants in soil and groundwater

- to study the interaction between organisms (soil fauna, bacteria, plants) and their chemical environment
- time dependence (ageing) of bioavailability
- cost effective procedures for estimating bioavailable fractions in the environment.

2 Fitness for Use

A) Human health risks

- validation of human exposure pathways
- availability of contaminants within the human body
- availability of contaminants in the soil as compared to the availability in the animal experiments underlying most toxicological reference values.

B) Ecological risk assessment

- impact of a site on its environment
- ecological recovery at the site
- changes in community structure caused by pollution-induced tolerance versus classical ecotoxicological endpoints
- biomagnification and adverse effects on food chains
- ecological soil quality requirements related to human land use.

C) Risk perception and communication

- Risk perception of contaminated land
- Development of communication strategies: how to communicate the results of risk assessments and the choice of solutions to those potentially at risk and to other interested parties.

D) Remediation Technologies

- Processes of natural attenuation
- Low-energy approaches
- cost-effective remedial technologies
- Monitoring of remediation

Why We Need to Act Now

In recent years we have made great strides in Europe in forging a common understanding of the problems left by our industrial heritage. It is now recognised that the emerging disciplines of environmental risk assessment and management are vital in helping us tackle the contaminated land problem.

Without these tools, and the decision-making framework in which they can be used, the costs of regenerating former industrial sites will continue to impose a severe burden on industry and the public purse. Some of the consequences of this are likely to be:

- continued dereliction which reduces quality of life and stigmatises affected communities
- a distorted and inefficient market in land which may have been contaminated
- increased pressure to develop greenfield sites
- lack of confidence on the part of investors, both in the technical solutions to deal with contamination and the potential regulatory obligations that developers or owners might subsequently face
- negative perceptions among affected communities which can lead to fears about health risks and environmental damage, and reduction in property values.

The CARACAS and NICOLE programmes have identified closely similar research needs. We know what needs to be done.

Now we must ensure that the research funding can be found to do it so that the benefits of a cleaner and safer environment can be achieved for future generations.

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Acknowledgement

The paper was prepared on behalf of the Concerted Action Projects CARACAS and NICOLE by C. Ferguson, J. Vegter, D. Laidler, M. Bell, B. Hafker, P. Bardos, J. Marsh, and H. Kasamas.

The Concerted Action Projects are funded by the European Commission DG XII within the EC Environment & Climate Programme, CARACAS is co-ordintated by the German Environmental Agency, NICOLE by ICI Research & Technology Centre, UK, and CLARINET by the Austrian Environmental Agency.

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

CONTAMINATED LAND REGULATION IN THE UK: THE RÔLE OF THE ENVIRONMENT AGENCY (EA) AND SCOTTISH ENVIRONMENT PROTECTION AGENCY

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Key words: legislation, authorities' rôle, prevention policies, regeneration

Summary

Section 57 of the Environment Act 1995 introduces a new contaminated land régime for the United Kingdom. Once implemented the new régime will provide a modern legislative framework for dealing with the historic legacy of land contamination in the UK. The Environment Agency (EA) and the Scottish Environment Protection Agency (SEPA), together with the Northern Ireland Environment and Heritage Service, will have specific new duties and powers under this new régime to supplement their general duties and existing powers and responsibilities relevant to contaminated land under other régimes. This paper summarises the rôle of the environment agencies in England, Wales and Scotland and outlines some of the objectives for the development of an integrated approach to contaminated land regulation.

Kurzfassung

Absatz 57 der Umwelttakte (Environment Act) von 1995 fuehrte eine neue Altlastenverordnung fuer das Vereinigte Koenigreich ein. Nach seines vollstaendigen inkrafttretens wird die neue Verordnung moderne legislative Rahmenbedingungen fuer das Aufarbeiten von historischen Altlasten bieten. Die Umweltbehoerde (EA) und die schottische Umweltbehoerde (SEPA), zusammen mit der nordirischen Umwelt- und Kulturbehoerde, werden genau definierte Pflichten und Befugnisse erhalten, um ihre allegmeinen Pflichten und bestehenden Befugnisse in bezug auf Altlasten unter der alten Verordnung zu staerken. Dieser Beitrag fasst die Rolle der Umweltbehoerden in England, Wales und Schottland zusammen, und erlaeutert Ziele im Zusammenhang mit der Entwicklung einer integrieten Altlastenverordnung.

Résumé

L'article du Loi de l'Environment (1995) impose un nouveau régime à propos de la terre contaminée en Royanne-Uni. Après son application, ce nouveau régime fournira un encadrement moderne et législatif qui s'occupera de l'heritage de la contamination de la terre en Royanne-Uni. Sous ce nouveau régime, L'Agence de l'Environment (EA) et l'Agence pour la Protection de l'Environment Écosse (SEPA), avec l'Agence de l'Environment pour l'Irelande de Nord auront les nouveaux fonctions et pouvoirs qui ajoutent aux pouvoirs et fonctions existants. Cet article résume le rôle des agences de l'Environment en Angletterre, le Pays de Galle et Écosse, et expose les gros lignes de quelques objectifs pour le développment d'une approche integrée envers la régulation de la terre contaminée.

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Contaminated Soil '98, Thomas Telford, London, 1998, 33–42

Introduction

The Environment Agencies. The Environment Agency (EA) and the Scottish Environment Protection Agency (SEPA) ('the Agencies') were established in primary legislation in the Environment Act 1995 bringing together the expertise of their predecessor bodies. Together with the Environment and Heritage Service in Northern Ireland (NI EHS), they represent the key environmental regulators for pollution control in the UK.

The EA and SEPA became fully operational on 1st April 1996 and are responsible for the protection and enhancement of the environments of England and Wales (EA) and Scotland (SEPA) and for making contributions to the goal of sustainable development through the integrated management of land, air and water. These Agencies are Non-Departmental Government Bodies, being accountable to the Secretaries of State for the Environment, Transport and the Regions, and for Scotland, respectively. The EA employs some 9 600 staff and has a planned 1998/9 budget of £195 million. SEPA employs approximately 650 staff with a planned 1998/9 budget of £26 million, these differences reflecting the differing sizes of organisation, the extent of responsibilities according to area of operation and the additional functions of flood defence, fisheries, recreation and navigation held by the EA. Contaminated land is one of the new areas of responsibility for the Agencies.

Contaminated Land in the UK. Land contamination[a] may be present in many sites in the UK as a result of waste disposal or previous industrial use. It is often associated with processes that are now obsolete. Even conservative estimates put the number of potential sites in the hundreds of thousands and a 1993 estimate suggested that between 100 000 and 220 000 hectares (ha) of land is potentially affected by contamination, this representing between 0.4% and 0.8% of the total UK land area[1]. The issue of land contamination has emerged over the last 20 years as an important one for the UK, not least as a result of a number of well-publicised incidents in the 1980's and 1990's, a growing corporate interest in environmental liability[2] and increasing development pressure. For example, recent government projections suggest a need for an additional 4.4 million more households in England in 2016 than in 1991, with an additional 0.3 million households required in Scotland by 2008 over and above the 1994 figure. Historically, these projections have been consistently underestimated[3]. An aspirational target of 60% regeneration of brownfield land to support these requirements has been suggested[4].

Government policy has developed[5], following the initial expression, by local authorities, of difficulties with the redevelopment of former industrial land in the mid-1970's, from establishment of the Interdepartmental Committee for the Redevelopment of Contaminated Land (ICRCL) through to the 1990 House of Commons Select Committee inquiry and subsequent legislation in the Environmental Protection Act, 1990 to the introduction of a modern legislative framework for contaminated land introduced by Section 57 of the Environment Act, 1995. A key outcome of this ongoing process was the publication of the 1993/4 policy review: Framework for Contaminated Land[6] (Contaminated Clean-up and Control: Outcome of Review[7], in Scotland) which established the future principles for UK contaminated land regulation, these being:

- maintenance of the 'suitable for use' approach;
- dealing with urgent and real problems in a orderly and controlled fashion;
- the creation of greater clarity and certainty than the law currently provides; and

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[a] **land contamination**: here, used in the broad context to refer to land *affected* by contamination

- replacement of the existing statutory nuisance powers with a modern, specific contaminated land power; with extension to Scotland of the statutory nuisance provisions already existing in England and Wales.

The outcome of the policy review formed the basis for preparation of the new contaminated land[b] legislation.

The Rôle of the EA and SEPA in the Regulation of Land Contamination

Legal Framework. The UK legal framework for land contamination is complex and remains under development. Criminal liability exists in respect of the illegal deposition of waste on land; of unconsented discharges from land to controlled waters; and in respect of the operation of a prescribed industrial process without authorisation. Statutory civil liability exists for the removal of illegal waste deposits; for clean-up or compliance with a 'works notice' under the relevant water legislation or following a breach of an authorisation to operate a prescribed process; or whereby contamination constitutes a statutory nuisance. Under common law, the laws of nuisance and of delict (in this case, negligence) are also potentially applicable[8]. The new statutory powers of Section 57 of the Environment Act 1995 are available only where the land is *not* suitable for its current use and are intended to deal with the worst cases of land contamination in the UK.

The Agencies have three main rôles in the regulation of land contamination:

(i) operating *existing* powers and responsibilities under pollution control functions to *prevent* land pollution;

(ii) advising on issues of site preparation and appropriate remediation, as a discretionary planning consultee to local authorities, on sites undergoing a change of use as a result of development planning; and

(iii) implementing the *new* duties and powers that will enable the Agencies to tackle the legacy of problem sites.

Existing responsibilities. The key existing responsibilities relevant to land contamination under the various pollution control functions or wider statutory powers are set out in Table 1.

In the main, the pollution control responsibilities are targeted at the regulation of issues other than land contamination and their ability to deal with the complexities of historic land contamination has often been compromised by the high burden of proof required. Greater success has been achieved through the environment agencies' rôle as a discretionary planning consultee, advising individual local authorities on the appropriate investigation and remediation of sites, and the ability of the agencies to influence the local area and regional structural plans of the local authorities.

The New Contaminated Land Régime. A new statutory régime specifically designed to deal with existing contaminated land was inserted in Part IIA of the Environmental Protection Act 1990 by Section 57 of the Environment Act 1995 but has not yet been implemented. Implementation requires a commencement order, Statutory Guidance, and Regulations on the operation of the new régime to be issued by the Secretaries of State. Under the proposed régime the primary regulatory rôle for contaminated land will remain with the local authorities. The Agencies will have new duties and powers to complement those of the local authorities, as detailed in Table 2 below. These will be in addition to the Agencies' existing responsibilities relevant to land contamination (Table 1).

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[b] **contaminated land**: here, specifically relating to the *statutory* definition of 'contaminated land' in the Environment Act 1995 (p.5) rather than the broader term 'land contamination[a]'.

Table 1: Key Existing responsibilities of the Agencies with respect to Land Contamination

Pollution control responsibilities	General responsibilities
• regulation of process industries • application of Integrated Pollution Prevention and Control (IPPC) Directive to installations regulated by the Agencies • regulation of radioactive substances • prevention or minimisation of pollution of the water environment • development of national regulatory policy for waste • ensuring effective implementation of new legislation relating to waste regulation	• advice on planning applications • dissemination of best practice • advice to Department of Environment, Transport and the Regions (DETR) (EA) and the Scottish Office (SO) (SEPA) • research and development • information exchange **Wider responsibilities** • to contribute towards achieving sustainable development • to have regard to the Agencies' conservation duties • to take into account the likely costs and benefits of its actions

Table 2: New responsibilities under s57 of Environment Act 1995

Environment Agencies (EA and SEPA)	Local authorities
Duties: • provide information to local authorities on land contamination • ensure remediation of special sites • maintain register of special sites remediation • prepare a national report on the state of contaminated land Powers: • provide advice to local authorities on identifying pollution of controlled waters • provide advice to local authorities on the remediation of contaminated land	Duties: • inspect their areas to identify contaminated land • consult the Agency on pollution of controlled waters • ensure remediation of land identified as contaminated • transfer 'special sites' to the Agency • maintain remediation registers

The new provisions follow through a sequence of actions involving:

- preparation, by local authorities, of a strategy to identify land in their areas that meets the statutory definition for contaminated land;
- inspection and identification by local authorities of sites which meet the definition; and
- action by local authorities or the Agencies, as statutorily defined, to secure the remediation of identified sites.

The statutory definition is: 'Contaminated land is any land which appears to the local authority in whose area it is situated to be in such a condition, by reason of substances in, on or under the land, that -

(a) significant harm is being caused or there is a significant possibility of such harm being caused; or

(b) pollution of controlled waters is being, or is likely to be caused'.

The Agencies are required to regulate those sites which are categorised as 'Special Sites', according to specific regulations; these regulations are intended to cover those types of contaminated land which the Agencies are already regulating through their statutory duties under other legislation, or for which the Agencies have particular expertise or knowledge. Statutory Guidance will support the primary legislation and provide further detail on how

local authorities and the Agencies are expected to implement their statutory responsibilities.

Management Arrangements for Land Contamination

In advance of implementation of the new provisions, the priorities for the EA and SEPA are the development of partnerships with local authorities and the regulated communities, the development of suitable training programmes for staff, the preparation of guidance documents to facilitate effective regulation of land contamination and technical support to the Department of Environment, Transport and the Regions and the Scottish Office on policy aspects and practical implications of the new contaminated land régime.

The Environment Agency. The Environment Agency in England and Wales manages its land contamination responsibilities through four main components:

(i) A central Land Quality policy team, part of the Environmental Protection (EP) Directorate, who focus on national and international policy and strategic matters concerning land contamination and broader land quality issues. The policy team also liaises with EP policy teams responsible for pollution control functions such as waste management, water quality regulation, radioactive substance regulation (who also deal with policy development on radioactively contaminated land) and process industries regulation, in the development of an integrated regulatory approach;

(ii) Regional and area management and technical teams who carry out the Agency's existing regulatory responsibilities and will be responsible for delivering the new duties and powers of s57;

(iii) National Centres, including Groundwater and Contaminated Land, and Risk Analysis and Options Appraisal, who provide technical expertise and strategic support to the policy teams and to the Regional and area teams; and

(iv) A National Land Quality Group, involving staff from the policy teams, Regions, the National Centre for Groundwater and Contaminated Land, the EP policy functions and SEPA; this group facilitates the development and dissemination of policies and practices for regulating land contamination Agency-wide.

Land contamination is one of the key areas where the Agencies can work in partnership with a wide range of other stakeholders to achieve a collaborative approach to develop both understanding and solutions. The Environment Agency has a particular rôle in working with local authorities to complement and support their duties under the new régime. The Environment Agency will be preparing, in conjunction with SEPA, specific protocols for the liaison and interface on land contamination as part of the development of arrangements under a Memorandum of Understanding, being prepared to establish the broad terms of cooperation and consultation between the Agency and local authorities. In addition, the Agency has set itself a number of specific tasks, including:

- influencing and informing policy and practice for dealing with land contamination and building partnership approaches, both nationally and internationally;
- encouraging or enforcing remediation of priority sites;
- agreeing protocols with local authorities to ensure that effective arrangements are in place for the provision of appropriate advice where there are joint responsibilities;
- developing our management policy for dealing with land contamination to ensure the coordination and integration of the Agency's various regulatory and other responsibilities;
- developing a quality management system and procedures for effective delivery of the regulatory and advisory function in land contamination;
- identifying standards of expertise, training needs and performance measures to ensure staff development and effective delivery of our functions in land contamination;
- providing high quality and appropriate technical advice on land contamination, based on

sound science, to encourage best practice and sustainable solutions;
- delivering a research programme to support our aims and objectives;
- establishing an information strategy which ensures effective data management as a basis for efficient information exchange, dissemination and analysis. In particular, the information strategy will support our regulatory and advisory functions and the preparation of a national report on contaminated land.

The EA's Land Quality Research Programme supports the Agency's aims and objectives in land quality and covers the following topic areas: (i) information; (ii) risk assessment; (iii) laboratory analysis; (iv) remedial treatment; (v) quality assurance; and (vi) research management and dissemination. The Agency achieves added value from its R&D programme by undertaking collaborative R&D and influencing other research funders. It is collaborating, or proposes to collaborate, in projects funded by government departments, CIRIA, development agencies, SEPA, SNIFFER (Scotland and Northern Ireland Forum for Environmental Research), the UK research councils, industry and the European Commission. The programme also takes account of work in other countries and of possibilities for the UK to influence and contribute to important international developments through involvement in, for example;
- the NATO/CCMS pilot studies on innovative remediation technologies;
- the EC concerted actions involving member states and academics on risk assessment (CARACAS) and remediation (CLARINET); and
- the industry-led EC concerted action (NICOLE), which provides a forum for industry problem holders and academic researchers to come together to find workable solutions to the problems of land contamination.

The Agency actively encourages the dissemination of information on R&D projects through papers and articles in the technical and scientific literature, and through seminars and conferences. Information on R&D progress and outputs is continually disseminated to the Agency's Regions and Areas through the Land Quality function.

The Scottish Environment Protection Agency. SEPA is arranging for management of its contaminated land responsibilities through the Environmental Strategy Directorate and through a SEPA centre of expertise in contaminated land, the rôle of which is :
- to provide technical and policy support to SEPA staff on the new contaminated land régime, as and when required but, in particular, on site identification, categorisation and remediation;
- to follow developments in contaminated land issues and ensure SEPA is current in the technical areas required for carrying out its statutory duties (e.g. risk assessment for contaminated sites, groundwater modelling, remediation technologies);
- to liaise across other business areas that impact on SEPA's contaminated land duties (e.g. groundwater protection, waste disposal and licensing, integrated pollution control and, in future, integrated pollution, prevention and control);
- to provide project management for SEPA and related research projects in contaminated land, where appropriate; and
- to prepare regional input to the national report on the state of contaminated land, as appropriate.

The centre of expertise will co-ordinate, develop and provide a focus for technical support to regulatory staff at a regional and area basis. The 'centre' will maintain regular external contact with the National Groundwater and Contaminated Land Centre, the environmental consulting community in Scotland and various industry groups with an active interest in contaminated land management. R&D is principally administered through the collaborative SNIFFER programme and SNIFFER's waste and contaminated land research

advisory committee (RAC).

Contributions to Sustainable Development

Land quality is a vital component of sustainable development. To progress in a sustainable manner, we cannot leave large quantities of land damaged, depleting its capability to fulfill its functions and meet our various needs. Bringing contaminated land back into beneficial use helps conserve land as a resource and reduces pressures on greenfield sites, thus conserving agricultural land and natural habitats.

The EA and SEPA will discharge their functions in accordance with the policy and approach set out in Ministerial guidance on sustainable development (for example, see Table 3 below). The Agencies recognise that dealing with the legacy of contaminated land is a considerable economic burden and that the objectives of sustainable development do not mean that contaminated land must necessarily be brought to a standard where it is fit for *any* purpose ('multi-functionality'). Instead, the aim in the UK, as in other countries, is to ensure that sites posing the largest risks are dealt with first, and that risks are assessed in relation to the use of the land concerned.

This 'suitable for use' approach will provide the basis for action both under the new contaminated land régime, where sites must be suitable for their current use, and within the planning framework, where sites are cleaned up for new uses. The Agencies will identify and promote the use of solutions for dealing with land contamination which follow the principles of sustainable development, in particular for conserving resources such as land and energy. The Agencies will also seek to prevent new damage of land, for example through waste management licensing and the Integrated Pollution Control régime.

The Agencies are also statutory consultees for Local Authority development plans and are able to provide advice and comment during plan preparation. Also, although not a formal statutory consultee on planning applications for the redevelopment of land which may be affected by contaminated, in practice, and as suggested Government planning guidance, the Agencies are consulted by local planning authorities on many applications through area planning teams (EA) and planning liaison officers (SEPA) who involve technical specialists as appropriate. This consultation process provides a major opportunity to influence development planning, land regeneration strategies and approaches to sustainable remediation at a local and site-specific level.

The introduction of the new legislation and the increasing focus of attention on contaminated land make it clear to developers that any scheme which does not address contamination adequately may result in the site becoming classed as contaminated under the new legislation. This should not be seen as a threat to development - the property market is increasingly seeing the opportunities for brownfield sites and has actively sought the certainty of a regulatory system so that they can assess sites and the associated financial implications.

Examples of EA and SEPA Regulatory Involvement

Financial arrangements for progressing remediation are different for England and Wales and Scotland.

Environment Agency. The Environment Agency is involved in a number of schemes throughout England and Wales through its planning responsibilities, through its duties to protect controlled waters and because of direct identification of problems or

Table 3: Contributions to the goal of Sustainable Development through SEPA's Regulation of Land Contamination

Principal Objectives (from Ministerial Guidance)	Contaminated Land Contribution
• *adopt, across all its functions, an integrated approach to environmental protection and enhancement, which considers impact of substances and activities on all environmental media and on natural resources;*	• develop an integrated approach to preventing, controlling and mitigating the effects of land contamination; • consider the range of regulatory controls open to SEPA across all media and adopt a consistent approach;
• *work with all relevant sectors of society, including regulated organisations, to develop approaches which deliver environmental requirements and goals without imposing excessive costs (in relation to benefits gained) on regulated organisations and society as a whole;*	• develop partnerships with those involved in the management of land contamination, emphasising prevention; • adopt a approach to remediation proportionate to the risks, costs and benefits gained;
• *adopt clear and effective procedures for serving its customers, including developing single points of contact through which regulated organisations can deal with SEPA;*	• develop transparent procedures for regulating land contamination at a local level; • provide single points of contact at local operational level and for contaminated land policy
• *operate to high professional standards, based on sound science, information and analysis of the environment and of processes which affect it;*	• conduct, sponsor and contribute to research that supports a sound scientific basis for the regulation of land contamination; • train relevant staff in appropriate aspects of contaminated land management;
• *organise its activities in ways which reflect good environmental and management practice and provide value for money for those who pay its charges and taxpayers as a whole;*	• develop transparent procedures for regulating land contamination at a local level; • consider the range of regulatory controls open to SEPA across all media and provide a consistent approach;
• *provide clear and readily available advice and information on its work; and*	• provide readily-available information on land contamination in line with regulatory requirements;
• *develop and close and responsive relationship with the public, local authorities and other representatives of local communities, and regulated organisations.*	• work, with others to secure the prevention, control and remediation of land contamination and its affects on the wider environment.

potential problems caused by land contamination. This year the Agency has bid for additional funds from the DETR through its Supplementary Credit Approval (SCA) scheme, to bring forward an initial group of sites causing pollution of surface or groundwater, for investigation and subsequent remediation, as appropriate. The SCA scheme (currently £14 million annually) is available to both local authorities and the Environment Agency, and is intended to allow sites to be investigated and remediated, where no other form of funding is available or appropriate, and where remediation is a priority. The Environment Agency will make annual bids for funds to deal with appropriate sites.

One such site is an abandoned landfill at Helpston, near Peterborough, for which the Agency are drawing up a remediation strategy. SCA funding has been secured for the first phase of work to develop the remediation scheme including a groundwater treatment plant. This pump and treat type plant which will serve not only the purpose of treating groundwater and but will also help in de-watering the site for subsequent civil engineering works.

Scottish Environment Protection Agency. In Scotland, there is no equivalent programme to SCA. Resources are made available to SEPA on a grant-in-aid basis (GIA)

and submissions to the Scottish Office would need to be made for individual remedial schemes on an individual basis.

In advance of implementation of the new contaminated land régime, SEPA has focused on actively progressing the remediation of contaminated sites that are causing pollution through operation of its existing regulatory and consultative powers through water, waste legislation and through its rôle as a discretionary planning consultee. There has been a notable increase in the use of innovative treatment technologies throughout Scotland within the last 2 years, these being applied in full consultation with SEPA.

An example of the collaborative approach adopted by SEPA is the ongoing remediation of the Young's Detergent works, a 28 hectare site at Pumpherston to the north-east of Livingston, West Lothian. SEPA and its predecessor bodies has had active involvement with the site for several years. The site was the centre for Scotland's oil refining industry at the end of the last century and is owned by Young's Paraffin Light and Mineral Oil Company Ltd (YPLMO), a wholly owned subsidiary of British Petroleum (BP). Throughout the second half of the last century, and the first half of this, oil shale was mined extensively across West Lothian. Initially, the shale was subject to distillation at or near the mines to produce a crude "retort oil". As the shallow mines became exhausted, a deep mining of the shale was undertaken and refining performed at one of three sites. Viscous tarry residues from this process were usually disposed of in hollows or ponds near to the sites. From 1948 onward, the Young's site was also used for detergent manufacture with oil refining eventually ceasing in 1962. The detergent works closed in 1993 and the majority of plant and buildings demolished.

Post-closure site investigations revealed two principal contaminant groups at the site - surfactants from detergent manufacture and hydrocarbons from the oil refining - both with further implications for land and groundwater contamination. In addition, the company agreed to make safe all associated tar ponds outwith the site identified from mining/ industrial records and aerial photographs. Several remedial options were examined for the site including: (i) incineration (ii) cement kiln (iii) specialised recycling; (iv) stabilisation; (v) bioremediation; and (vi) landfill. Of these options only bioremediation and cement grout stabilisation were shown to be effective and are being pursued within the legislative framework of the existing waste management licence and with amendments to its conditions.

Tar residues from the oil refining process classed as 'soft' tars and having a relatively low polyaromatic hydrocarbon (PAH) content, are easy to work and become mobile when warm. These tars have been demonstrated as being suitable for biological treatment. Trials showed an initial 50-60%^{w}/w reduction in most contaminants due to the initial bulking process rising to 85-95%^{w}/w within 8 weeks of treatment commencing. A staged risk assessment, including the derivation of site-specific health-based remediation criteria, was conducted in full consultation with SEPA to determine acceptable final concentrations of key contaminants, most notably the more carcinogenic PAHs which were known to be present, commensurate with the final intended use for the site as an extension to the adjacent golf course ("suitable for use"). From the bioremediation trials it was estimated that all target concentrations would be achieved in 3-4 months of full scale treatment. Full scale treatment operations are now underway.

Hard tars from the refining process (probably polymerised soft tars), tars from the detergent sulphonation process and a high phenol tar from an adjacent site (possibly a gas works tar) were not suitable for bioremediation. These materials are being treated using an ex-situ grout-based stabilisation process. Ultimately, it is intended that the site will be restored to a level suitable for use as a golf course with the bioremediated material and

imported top-soil being used as a cover for the existing land. Secondary containment is provided by an existing cut-off drain and treatment system.

Partnership approaches between SEPA and the regulated community in Scotland have been adopted across all the SEPA Regions but notably for the remediation of waste material at an aluminium smelter (ex-situ bioremediation), for the licensing of a state-of-the-art engineered containment facility for former steelworks wastes, for the treatment of diesel-contaminated soils at a offshore fabrication yard (ex-situ bioremediation) and for the pilot-scale treatment of former tank farm residues (in-situ bioventing and biosparging). The partnership approach is consistent with both the forthcoming provisions of the Environment Act 1995 and with the wider aims of both environment agencies with respect to securing, with others, the remediation of contaminated land.

Conclusions

Both the Environment Agency and SEPA aim to secure, with others, the remediation of contaminated land, through their direct and indirect regulatory responsibilities. Within this aim, and in the context of contributing towards sustainable development, the environment agencies will:

- promote the appropriate remediation of contaminated land;
- regulate 'special sites' efficiently and effectively; and
- report on the state of contaminated land.

To achieve this, the Agencies recognise the need for, and place great importance on, building partnership approaches with other regulators, 'problem-holders', professionals and other interested parties. Partnership, underpinned by sound science and best practice technical approaches, consistent regulation and government support, can lead to more effective, sustainable and rapid progress in the remediation of unsightly and potentially hazardous sites.

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THE GERMAN FEDERAL SOIL CONSERVATION ACT - ENCOUNTERING THE CHALLENGE OF SOIL PROTECTION AND REHABILITATION OF CONTAMINATED SITES

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Key words: Legislation, national binding values, remedial measures, remedial investigation, remediation plan.

SUMMARY

The Federal Soil conservation Act will create the conditions for effective soil conservation and the clean-up of contaminated sites.

The Ordinance on Soil Conservation and Existing Contaminated Sites (*Bodenschutz- und Altlastenverordnung*) will contain regulations detailing requirements for remedial measures, remedial investigation and the contents of the remediation plan.

KURZFASSUNG

Mit dem Bundes-Bodenschutzgesetz werden die Voraussetzungen für einen wirksamen Bodenschutz und die Sanierung von Altlasten geschaffen. Die Bodenschutz- und Altlastenverordnung wird bundesweit einheitliche Anforderungen des Gesetzes an die Untersuchung und Bewertung von Flächen mit dem Verdacht einer Bodenkontamination oder Altlast konkretisieren, Sicherungs-, Dekontaminations- und Beschränkungsmaßnahmen näher bestimmen sowie Anforderungen an die Sanierungsplanung im einzelnen festlegen.

RÉSUMÉ

Contaminated Soil '98, Thomas Telford, London, 1998, 43–50

Une protection efficace du sol suppose l´ existance d´ instruments juridiques au niveau fédéral, régissant tant la prévention de contaminations futurs du sol que la réhabilitation des sols contaminés. Le projet de loi fédérale relative à la protection du sol crée le cadre juridique pour résoudre entre autres le problème des sols contaminés.
L´ ordinance de la protection du sol et pour des sites contaminés *(Bodenschutz- und Altlastenverordnung)* concrétise pour le site suspect de contamination ou le site contaminé les exigences unitaires concernant les methodes de réhabilitation, l´ investigation et de la planning de la réhabilitation.

1. Federal Soil Protection Act

In Germany special efforts are required to conserve the quality of soils in the long term. All environmental burdens - air pollution, contamination of waters, wastes and the depletion of land through surface sealing and building developments - affect the soil. Soil protection therefore constitutes a cross-sectional task for all environment policy measures. At the same time, soil protection represents a separate task in its own right.

The medium of the soil requires the same degree of legal protection as is today quite self-evidently applied to water - in the form of the Federal Water Act *(Wasserhaushaltsgesetz)* - and the air - in the form of the Federal Immission Control Act *(Bundes-Immissionsschutzgesetz)*. Piecemeal soil protection provisions in various types of legislation which embody the idea of soil protection must be expanded by central, medium-specific protective legislation which lays down concrete principles and clear obligations for action in the field of soil conservation.

At the moment around 190,000 areas suspected of contamination are recorded - around 85,000 each for the old and new *Länder*. The exact number of 190.716 sites includes 87,444 abandoned waste disposal sites and 103,272 abandoned industrial sites. The actual figure represents the status of inventory of sus-

pected contaminated sites excluding military contaminated sites and former armament production sites. An important contribution to economic development is made by solving the problem of contaminated areas. Often, for example, suspected contamination puts a block on urban and economic development. Binding requirements could help remove the suspicion of contamination from sites which are only slightly damaged, thereby releasing them for other uses. In areas of higher contamination, this would also faciliate a more accurate calculation of how much clean-up work is required.

The **Federal Soil Conservation Act** (*Bundes-Bodenschutzgesetz)* sets nationally uniform standards for effective soil protection and for averting hazards posed by contaminated sites. It is to become the basis for regulating the use of land in the case of harmful changes in the soil e.g. the suitability of building land for the construction of homes or of agricultural land for the cultivation of food. The importance of these provisions - not only for environmental protection but also for the equal legal and economic treatment of all areas throughout Germany - makes it necessary for nationally uniform soil values and protection standards to be specified. The Parliament (*Deutscher Bundestag*) has passed the bill on 12 June 1997. After the Federal Council (*Bundesrat*) has appealed the Conciliation Board (*Vermittlungsausschuß*) on 4 July 1997, the mentioned board has presented a consensual proposal.

At the heart of the Act are the duties to avert soil damage. The Federal Soil Conservation Act contains different commitments in the field of soil protection. Compliance with these regulations may be enforced legally. Existing damage (including abandoned polluted areas) must be removed as far as possible and reasonable), this also applies to the pollution of groundwater caused by the soil damage. In line with the „polluter pays-principle" the person who caused the contamination is held responsible, including the successor in interest. Besides the polluter, the owner or occupier is responsible as well. There is no legal precedens.

The complementary provisions on the clean-up of contaminated sites, that is closed landfill sites, illegal waste dumps and former industrial areas, form a particularly important part of the bill. In particular, the following is planned:

- The competent *Land* authorities are responsible for the identification, investigation and evaluation of all areas suspected of contaminiation.

- Self monitoring and notification are complementary to the official monitoring of contaminated sites and suspected contaminated areas.

- Procedural management will include being able to require those responsible for clean-up to produce a clean-up plan. To speed up the process a „*concentration effect*" was introduced for official decisions. An approved clean-up plan or an official clean-up order is to include the necessary official approval. Therefore further official procedure for the licensing of soil clean-up plants in line with immission control legislation or for authorisation in line with water legislation will be unnecessary.

- The responsible party may submit a draft clean-up contract with the clean-up plan.

- The responsible parties must inform those concerned on forthcoming clean-up measures in good time.

Together with the clean-up of soil and contaminated sites the clean-up of waters polluted by contaminated soil will henceforth be regulated by Federal legislation. From now on it will be possible for the clean-up procedures to be more effectively and speedily carried out.

In Germany, responsibility for identifying, assessing and cleaning up existing contaminated sites generally lies according to the German Constitution with the 16 Federal *Länder*. As long as Federal legislation does not exist, the *Länder* have the right to proclaim their own legislation in this field. In three *Länder* soil

conservation acts have already been enacted. Most of the *Länder* have introduced provisions - with varying degrees of thoroughness - to cover the issue of abandoned polluted sites. The need for a Federal Soil Conservation Act can be deduced from the fact that currently the competent authorities of the *Länder* have 37 remediation lists at their disposal, to determine the individual remedial objectives. As every authority has one list which it uses as its own binding guideline, enterprises with business activities in all 16 *Länder* have difficulties to cope with this proliferation of lists.

2. Establishment of detailed requirements in regulations issued under the Federal Soil Protection Act

To ensure a nationally uniform approach, precise requirements will be specified in an **Ordinance on Soil Conservation and Existing Contaminated Sites** (*Bodenschutz- und Altlastenverordnung*) to be adopted by the Federal Government.

The Federal Soil Protection Act confers authority to issue regulations detailing requirements for remedial measures, remedial investigation and the contents of the remediation plan.

2.1 Requirements concerning the nature and extent of remediation of contaminated sites and of harmful changes to soil

In keeping with the obligation to avert impending danger, the remediation of contaminated sites and of harmful changes to soil must be carried out so as to permanently ensure that any residual pollution that might remain does not result in dangers or considerable nuisances for individual persons or the public at large. For containment measures in particular, this means that danger can only be considered as having been eliminated on a permanent basis if the measure

is effective for the long term and if its effectiveness can be monitored. Depending on the effectiveness of the remedial measure and the expenditure it involves, requirements can be stipulated as required in the case concerned, and in consideration of the principle of proportionality.
Decontamination measures always meet these demands. In individual cases, a permanent elimination of danger can also be achieved through containment measures, provided that technical failure can be ruled out for the long term and with sufficient certainty, thus resulting in reliable protection of human beings and the environment.
Decontamination is normally the more reliable and hence the better way to achieve lasting protection, provided the measures used to this end are environmentally compatible.

Only in cases in which the averting of danger by decontamination or containment is not technically feasible or not reasonable can protective measures be taken or restrictions be imposed.
In examining the suitability and effectiveness of a measure in a given case, the use of the site as permitted under planning law as well as the resulting protection needs must be taken into account. The only case in which the use of the site is not a decisive factor is the rehabilitation of water bodies.

2.2 Requirements for remedial investigation and the establishment of remediation objectives

In cases in which an abandoned site poses a particularly grave hazard to human beings and the environment, site conditions are complex and several contaminants and exposure pathways are present, remedial investigation is an important element between final hazard assessment and the actual performance of the remedial measure. The object of remedial investigation is to select from the multitude of available remediation options those measures or combinations of measures which are technically feasible, appropriate, reasonable and

legally permissible in the case concerned. Remedial investigation is normally composed of the following elements:

- description of site conditions
- definition and justification of remediation objectives
- examination of possible variants, performance of a feasibility study if necessary
  (definition of remediation zones; selection of basically suitable remediation techniques/processes; performance of preliminary suitability tests, if necessary; development of remediation scenarios; estimation of cost and time frame)
- proposal of suitable measures or combinations of measures (remediation proposal).

2.3 Requirements for the remediation plan

The remediation plan must set out the envisaged remediation concept in a verifiable manner and contain the necessary information and documentation, including that needed by the authorities for decision-making. Based on remedial investigation, the remediation plan serves as the technical basis for the official order to carry out contaminated site remediation as well as for authorisations that may have to be obtained under other legislation, such as a license for soil treatment plants under immission control legislation.

The scope of the remediation plan and the type and detail of the information to be provided in it may vary depending on the case concerned. The remediation plan should in principle contain the following information:

- general description of the remediation concept (measures, construction and earth moving work, disposal of residuals, etc.)
- detailed information on the various measures (calculations concerning treatment in plants, in-situ measures, containment elements)

- demonstration of suitability (attainability of remediation objectives)
- information on investigations accompanying the remedial work and on quality assurance (re-incorporation, etc.)
- after-care and surveillance
- cost and work schedule

THE USE OF RISK ASSESSMENT AND RISK MANAGEMENT IN THE REVITALIZATION OF BROWNFIELDS IN NORTH AMERICA: A CONTROLLED OPENING

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Key words: abandoned polluted areas, authorities' role, environmental policy instruments, liability, risk management

SUMMARY
The concern for contaminated soil emerged at the beginning of the 80's. Since then, it never faded out, even if the interventions' focus changed many times. In North America, it is now on the redevelopment of "Brownfields", abandoned industrial and commercial facilities where expansion or redevelopment is complicated by environmental contamination. In the last years, new regulations, were adopted by governmental authorities to foster their reuse. Among them, some transcontinental trends can be perceived. The controlled use of risk assessment and risk management is one of them.

KURZFASSUNG
Verseuchte Böden sind zu Beginn der achtziger Jahre eines der Hauptprobleme geworden. Seitdem haben die Überlegungen und Interventionen dazu nicht nachgelassen, wenn auch deren Focus sich mehrere Male geändert hat. In Nordamerika liegt zur Zeit der Schwerpunkt auf der Wiederaufbereitung der "Brownfields", jener verlassenen Industrie- oder Wirtschaftsterrains, deren Wiederbenutzung durch reelle oder angenommene Verseuchung schwierig geworden ist. Im Verlauf der letzten Jahre haben die verschiedenen Regierungen durch die Einführung neuer Bestimmungen, Politiken oder Programme diese Tendenz der Wiederaufbereitung angeregt. Eine Analyse dieser Programme läßt bestimmte transkontinentale Tendenzen erkennen. Die kontrollierte Nützung der Risikoanalyse und die der Maßnahmen zur Verwaltung des Risikos sind eine davon.

RÉSUMÉ
Les terrains contaminés sont devenus un sujet de préoccupation majeur au début des années 80. Cela ne s'est jamais démenti par la suite, bien que le focus des interventions ait lui changé plusieurs fois. En Amérique du Nord, il porte maintenant sur le redéveloppement des "Brownfields", des terrains industriels ou commerciaux abandonnés dont la réutilisation est rendue difficile par la présence, réelle ou supposée, de contamination. Au cours des dernières années, de nouveaux règlements, politiques ou programmes ont été mis en place par divers gouvernements pour susciter ce redéveloppement. L'analyse de ces programmes révèlent certaines constantes transcontinentales. L'utilisation contrôlée d'analyses de risque et de mesures de gestion du risque constitue l'une d'elle.

Contaminated Soil '98, Thomas Telford, London, 1998, 51–59

The industrialized world became conscious of the problem resulting from the uncontrolled massive burying of industrial waste and the resulting impact on soil and ground water at the beginning of the 80's Spectacular and mediatised cases, Lekkerkerk in the Netherlands, Love Canal in the United States, Ville LaSalle in Canada were more then enough to change the perceptions and the way of doing things. Following those events, it took only some years for different countries, provinces, states or länder to adopt regulations or policies aimed to curb the problem. But, over the years, the number of cases discovered grew almost exponentially. The regulations and policies targeting contaminated soils had to be modified, extended, complexified, to cope with new situations and concerns.

This set of events is now going on since almost 20 years. During this time, the main focus of the intervention changed. Today, in North America, it is on the revitalization of Brownfields. Recently, a whole new set of regulations, policies or programs has been issued by various governmental authorities to cope with this particular problem.

In Quebec, the revision of the 1988 *Rehabilitation Soil Policy* was initiated in 1994. While working at it, we did an extensive revision of what was going elsewhere in North America, in different other Canadian provinces and American states. This paper is a summary of our findings.

A Moving Focus

At the beginning of the 80's, contaminated sites numbered by the hundreds in each provinces or states. In the province of Quebec, the Inventory of Hazardous Waste Contaminated Sites, first published in 1984, showed 311 cases. At that time, the American Superfund National Priority List had less then 500 sites. The contaminated soil problem appeared quite small and manageable. A contaminated site was perceived as a hole in the ground were industrial waste (barrels, sludge, liquids) had been eliminated The main preoccupation was to make sure that those waste were under control, that the contaminants were not seeping through the underground to pollute the ground water and impact the health of the surrounding inhabitants or the environment. Remediation appeared quite straightforward: containment through physical barriers or capping, groundwater pump and treat to achieve the full decontamination of a site or, eventually, for some sites, the removal of the waste.

Directly related to this concern was also the necessity to make sure that the contaminated sites would be cleaned up by the polluters and not be transferred to governmental authorities or innocent third parties. In the U.S., the Superfund was created with this aim in mind and some states adopted tough regulations to prevent transfer of contaminated properties The model for these regulations is the New Jersey *Environmental Cleanup Responsibility Act* (ECRA) adopted in 1983, a program, who legally forced the owners and operators of an industrial establishment that uses hazardous substances or wastes to "remediate" their property as a condition to selling or transferring the business or property.

Even if they still exist today, those concerns were rapidly relayed to the background, in Canada at least, as a new focus emerged. The industrial upheaval of the 80's induced the closure or relocation of many industrial plants. Located in or close to city centers, along waterways or near trendy areas, well deserved by all kind of infrastructures and relatively cheap, those sites acted as magnets for developers. New residential, commercial, light industrial or recreational areas were planned on pieces of land which had been used for decades by heavy industries.

Site's characterisations revealed a major problem: many of those sites were contaminated. This contamination resulted not always from the intentional burying of waste, but also from all kind of miscellaneous sources; inadequate storage area, deficient underground storage tanks or transbordement practices, air deposition, etc.. The picture of what was a contaminated site expanded, to include all former industrial sites. Potentially at least, contaminated sites suddenly numbered by the thousands. And the main focus for soil policies became how to prevent the reuse of former, still contaminated, industrial properties.

As Quebec, Ontario and British Columbia adopted their respective soil rehabilitation policies at the end of the 80's, this concern was already in the foreground. Thus, the focus and major goal of those policies were to guide the developer toward the safe reutilization of contaminated land and, if impossible, forbid it. Meanwhile, at the same time, those policies made clear that it would be counterproductive to fence the contaminated lands and discourage all reutilization projects. A delicate balance had to be crafted out between contaminated sites reutilization and the protection of their future inhabitants

This balance was provided by the introduction of generic cleanup criteria and the concept of functionality. The extend of the decontamination would depend on the sensitivity of the future use, agricultural and residential uses being more critical then commercial and industrial uses and needing a more extensive cleanup. Still, the main idea of this strategy was that, to be reused, a contaminated property had to be formerly cleaned up, if not totally, at least extensively.

To get there, the regulators counted on the power of the market. In a period of relative economic prosperity, it was believed that clear clean up goals and the magnetism of profit magnetism would be enough to foster the cleanup of polluted sites by developers, at least for the well located urban sites.

But, by the mid 90's, this had to be reassessed. A new focus replaced the former one: the Brownfields redevelopment.

The Brownfields

The term Brownfields was first coined in the United States. Even if all authorities do not exactly agree on what is exactly a Brownfield, the most accepted definition appears to be the following: *Abandoned, idled or under-used industrial and commercial facilities where expansion or redevelopment is complicated by real or perceived environmental contamination.*

The emergence of this new focus was directly related to the success of the former governmental initiative to curb the reuse of non decontaminated sites1 To be sure that the soil they planned to build on was safe, promoters, institutions, cities, governments, lenders and industrialists forded more and more site characterisations. The number of contaminated sites grew steadily. Whole sections of older cities appeared contaminated because, at some time in their history, the ground they stood on was levelled using all kind of material including incinerator ashes, slag's and demolition residues. Other areas were contaminated because the paints applied for decades on houses was leaded and had polluted the soil as it peeled off.

Forced to build on `"clean soil" before redeveloping, developers, lenders and potential buyers got nervous with the unpredictable costs and liability. As the economy slowed down, "Greenfields", undeveloped and uncontaminated agricultural land or forest , located in the suburbs or even further, became more and more an option. The investors deserted slowly the contaminated sites and the city centers, leaving behind towns deprived of revenues, idled and impoverished areas. Contaminated soil, or even the shadow of it, fuelled an already devastating trend, the urban spreading, recognised lately as one of the major social and environmental problem of the present time.

The following numbers give an idea of the extent of the problem. The U.S. General Accounting Office estimates that there are 130 000 to 450 000 Brownfields sites in the U.S., with potential clean-up costs of $650 billion. In the City of Chicago alone, 18% of industrial areas are unused, which is more than 1 500 acres spread among 2 000 sites.

To counter this phenomena, a new and even more difficult balance had to be worked out. On one side, Brownfields should be redeveloped but, the cost of doing so should be held

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1 In the U..S. one more reason explaining the emergence of this concept is the will of the States to set a dividing line between what could be described as "minor cases", numbering by the hundred of thousands, mostly deal with at the States level, and the Superfund heavy type cases for which there is a great federal government involvement. As we will see further, due to its implication on the liability, this distinction plays a major role on the possibility to foster the redevelopment of Brownfields. In Canada, this factor played no role in the emergence of this new focus, as the federal government is much less involved in the cleanup of contaminated sites then in the U.S.

low and investors and new owners should be spared the liability of the past contamination. On the other side the health of the new users and the environment should still be protected and the governmental authorities should not become liable for everything left on site.

In the last three years, many Canadian Provinces and American States devised and promulgated new regulations, policies, programs and tools aimed to achieve this goal.

The New Approaches Aimed to Foster Brownfields Redevelopment

A review of those new approaches shows some transcontinental trends. The followings appear to be the major one:

- The adoption of functional generic clean-up criteria based on risk assessment;
- The possibility for the owner to select other cleanup strategy than the decontamination to the generic criteria, allowing them to leave more contamination in place;
- Multiple obligations for those who rely on risk management measures and are leaving contamination in place.
- Some governmental sign off conditions and liability provisions

The Adoption of Functional Generic Cleanup Criteria Based on Risk Assessment

The necessity for different sets of generic cleanup criteria devised according to the sensibility of different uses or settings is now largely acknowledge in North America. The existing criteria are mostly risks based, devised using generic exposure scenario for different uses. They consider, besides the risk on the human health, the impact on groundwater. Often, different sets of numbers exist for taking into account the depth of the contamination or the proximity of groundwater.

Some jurisdiction also consider the ecotoxicological risks for establishing their generic criteria Although this aspect is a growing concern, it is still yet far from being included everywhere.

Specific Risk Assessment and Risk Management: a Controlled Opening

Besides using generic criteria as a clean up goal, Brownfields owners or developers have the possibility to select other alternative risks management options as :

- doing a specific risk assessment and devising specific cleanup criteria adapted for a specific site and redevelopment project;
- leaving the contamination in place and using different passive or active risk management measures to contain and control the contamination, while allowing the reuse of the site;
- leaving the contamination in place and restrict, through institutional measures, problematic uses.

This opening is perceived by many as "the" major breakthrough for contaminated sites redevelopers, because it allows a lesser cleanup level then the one resulting from the application of the generic criteria, meaning that the cost for redevelopment is considerably reduced.

Even if, as we will see later, things are more complicated than that, there is indeed a clear concern among regulators that this opening could fire up an uncontrolled wave of inadequate projects2 , with many undesirable side effects, the least not being the increased risks for the health of the future inhabitants or the abrupt dismantling of the treatment facilities network patiently build up during more then a decade.
This explain the ambivalence felt in many documents on those alternative approaches. They are seldom presented as "the" solution and not always available without further reflection. Oregon for example, states that they are accepted but that it is not foreseen that they will be use routinely. Ohio accept them only if generic criteria or risk based site specific criteria could not be technically achieved or if the costs of rehabilitation exceed the economic benefits. Moreover, the alternative applied must have some positive impact on the quality of the environment.

Quebec considers not to allow alternative approaches for residential development were future users would have their own backyard, judging that the indispensable control needed to preserve the integrity of the risk management measures could then not be guaranteed. New Jersey for its part does not allow leaving the contamination in place if the cost of removing it is less then two times the costs of letting it in place And so on.

Besides those general statements, mechanisms are build in to insure that those who did manage the risk while living the contamination in place are not simply escaping their responsibilities and transferring their problem to innocent third parties. Those obligations, as diverse as site registration, bound service contract with the government, neighbourhoods consultations or newspapers advertisement, are inherent to the site specific risk assessment option. Closely linked to the long-term liability, public transparency and the necessity to guarantee the permanence of engineered confinement measures in a constantly changing world, those obligations often act as a deterrent for many developers and are strong incentive for the use of generic cleanup criteria.

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2 This fear may be unjustified. Although British Columbia is giving, since 1988, developers the choice between removal and in-place management of the contaminants, this later option was selected for only 5% of the sites. Many purchasers do not want to buy contaminated property out of concern for long-term liability.

The Registration of the Remaining Contamination and Risk Management Measures

Prior to the reuse of a contaminated sites were contamination had been left in place, most governmental authorities now require some types of registration. This act as a memory and a warning for actual and future owners, purchasers and neighbours. It is perceived as a *sine qua non* condition to insure transparency when the transfer of such properties occurs, to maintain the appropriate engineered confinement measures and use restriction, and to protect the public and the environment. Most regulators opt for a registration on the land title. Some, like British Columbia for example, have devised a special computerising inventory accessible by the public.

Bound Service Contract with the Government

In most cases, even if participating in a voluntary program, the owner of a contaminated site will need some kind of governmental agreement to proceed with alternative risk management measures. Bound service contract, between the owner of the site and the government are currently compulsory. In this agreement, the owner will extensively describe the engineered measures he had to maintain on the site to control the risk, the follow-up he must commit to and the land use restrictions he must obey. Financial guarantees may be asked for. The bound service contract is often registered on the land title.

Neighbourhoods Consultation and Newspaper Advertisements

Moved by the concept of transparency, some regulators gave the public the possibility to get involved in the decisions concerning the contaminated site. In Ohio, terms and conditions of alternative measures cannot be defined without a public consultation. Pennsylvania requires for its part that notices first showing the intentions of the owners, then summarising the final report, be sent, to the municipality concerned and published in a local newspaper.

The Governmental Sign-off

More then the opening to alternative risk management measures, the governmental sign-off or approval could be the major piece of the Brownfields redevelopment puzzle. This is a part which regulators, sites owners, developers and the public are very sensitive to3. It has a direct impact to past, present and future liability and will grandly determine the confidence which buyers will have in the whole process. If they feel that they could be left alone in case of unforeseen problem, they will engage reluctantly in the process. Thus, regulators are divided between the need to devise approaches which will persuade other parties to step forward an initiate a process leading to reuse, while keep some viable responsible party "on the hook". Some regulators will give up one of these goals in order to persuade developers to finance the cleanup.

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3 This is even more true in the United States, were all contaminated areas could, in theory , land on the Federal Superfund National Priority List, meaning that a wide range of persons, including new owners or lenders, could be held accountable for the site cleanup, disregarding any previous agreement with states authorities.

Generally, regulators are easily willing to recognise the quality of the work done, be it the full cleanup of the site or some alternative risk management measures. Often, in this later case, only a conditional certificate of compliance may be given, valid as long as mitigation measures are kept in place. The owner of the site may have to prove that the property is still safe after a period of time to keep its certificate.

Sometimes, the system can become quite elaborated. In Minnesota for example, there are no less then five types of assurances:

- technical assistance or approval letters, who as no assurance connected with them at all except review from the Environmental Protection Agency and a letter saying that this was conducted in a competent manner and that the agency agree with the conclusions of the consultant who was conducting the works ;
- a no-action letter or agreement, meaning that the government has no more interest in the site and will not take any new actions (in the absence of new facts);
- the off-site source determination or good neighbour letter or agreement saying that the contamination founded on a site is coming from elsewhere;
- the certificate of completion if cleanup was performed;
- the no association to past contamination letter, meaning that the activities going on the site has nothing to do and do not interfere or will not interfere with already existing contamination.

Covenant not to sue are also given by some regulators.

Generally, regulators will put some responsibility on the owners and its consultants for undiscovered or unreported contamination, incomplete cleanup or bad risk management practices. In such cases, the owner will be held responsible for any damage to the human health, the goods or the environment.

It is impossible to say yet which form of assurance is working or not working. But in the opinion of the regulated, it seems that even a small forms of assurance is already a major source of motivation for many developers.

The Impact of the New Policies on Brownfields Redevelopment

Most of the policies or programs aiming to foster Brownfields reutilization are only a couple of years old and it is still too early to assess their full impact. There is already examples of reused sites, who would probably not have been redeveloped using generic cleanup criteria alone. On the other hand, cleanup to generic criteria is for many buyers, still the only acceptable and safe solution. Ultimately, it is the confidence of the market who will judge the viability of those new measures. This confidence build-up will rely on the seriousness of the risk assessment studies and management measures realised and on the commitment of the regulators.

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INDUSTRIAL POLICIES AND STRATEGIES

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Keywords:

authorities' role, clean-up cost, environmental management, liability, management, policies, practice, prevention, risk management, soil and groundwater contamination.

Summary (English)

The objectives of industry to comply with legal requirements, to protect human health and the environment and to manage liability issues require a strategic approach of risk management when dealing with contaminated land. This should include prevention of on-going contamination, a systematic approach to historic contamination, and ensuring the availability of appropriate technology. The approach to Land Protection is an integrated part of a company's environmental management.

Contaminated Soil '98, Thomas Telford, London, 1998, 61–64

INTRODUCTION

Manufacturing industry is diverse and produces a wide range of products. Manufacturing sites vary in size from small, single process facilities to large multi-company multi-process complexes. The mix of chemicals processes on site involves the handling of a variety of organic and/or inorganic substances.

Many of the sites have been used for manufacture since the 1800s, and have supported a variety of different industrial processes. They are therefore likely to be contaminated to varying degrees by a number of different contaminants. In addition, some of the sites are located in residential areas and/or adjacent to important water courses. This complex mix of sensitive targets and potentially problematic land contamination means that sites are best dealt with using a site specific risk based approach.

In dealing with contaminated land the objectives of industry are to:-

- safeguard health and the environment
- comply with legal requirements
- ensure liabilities associated with acquisitions, and sale and transfer of land are fully understood, and
- ensure that soil and groundwater contamination is dealt with in the most effective way.

These objectives are met by a positive approach of understanding, assessing and managing the site specific risks associated with contaminated land.

Prevention

However, before even considering how to deal with historic contamination, the highest priority must be given to the prevention and containment of on-going contamination. Prevention is not only more cost effective than attempted clean-up, but also is rightly given a higher priority by regulators, insurers and other stakeholders. Industry must therefore be able to demonstrate that we have the relevant management processes in place to ensure that prevention of on-going contamination is actively pursued and regularly audited. In particular, very small amounts of contaminants entering groundwater can cause very large volumes of water to be unfit for use, with high costs and serious practical difficulties in attempting its remediation. There is therefore a strong incentive to prevent contaminants entering the ground.

Best practice followed by industry should ensure that all the different stages of the life of a manufacturing plant are considered; design, commissioning, operation, decommissioning and demolition. Additionally, the use and final disposal of the product will also be examined.

At the design stage the plant siting, its layout and detailed design should all take into consideration as far as is practicable the protection of ground and groundwater. At this

stage it is often possible to build in additional protection at marginal cost. When the plant is operational then it is important that the original design intent is maintained for any modifications and that adequate asset maintenance is carried out. At the stage of decommissioning and demolition the programme of work should ensure that ground protection is considered during all phases of the work making due allowance for the many temporary situations of storage of waste materials. Each site will have clear management responsibilities covering these areas ensuring that appropriate procedures are in place.

Most sites were designed and built at a time when the effects of ground contamination were not recognised, even though best practice was followed at the time. In most cases, the containment performance of these plants is most cost effectively improved by a systematic programme of adopting rigorous procedures for operation and maintenance, together with a long term programme of auditing to ensure the procedures are being followed.

Historic Contamination

Today, much is known about the causes of historical land contamination. Primary sources of contamination are leaks from underground storage and drainage spills, leachate from unlined lagoons and landfills, poor housekeeping, and uncontrolled demolition.

Steps have been taken by industry to eliminate sources and potential sources of contamination by improving existing facilities and operating practices, and improving the design of new facilities. Historical land contamination has been dealt with by adopting a systematic approach to assessment and remediation. The approach used varies from company to company but typically involves a desktop study to identify potential contamination on site followed by a site investigation to characterise the contamination and a risk assessment to determine its significance in terms of potential to cause harm to health and the environment. In this process use is made of the source-pathway-receptor scenario concept which also provides a sound basis for identifying appropriate remedial options if needed.

Technology and Research

Our experience is that while it is possible, when appropriate, to deal with 'hot spots' of contaminants in the ground there are few effective technologies for remediation of large areas of more diffuse contamination or where the contaminant has affected large volumes of groundwater. In these cases source destruction or removal is often not feasible or extremely costly, and we therefore seek out cost effective containment.

Industry is committed to research and develop lower cost, effective clean-up strategies and we have found that for most manufacturing companies research into contaminated land is not seen as a competitive issue. This has enabled the formation of many consortia and networks aimed at sharing the costs of research and technology development, and the

work of some of these is described later in this conference. One of the problems facing research institutions is the difficulty of scaling up from the laboratory to field scale implementation and it is in this area where public/private collaborations can be useful.

Management Strategy and Policy

This systematic approach to understanding and managing the specific issues on a particular site has to be underpinned by a comprehensive management strategy. The strategy must enable the problem holder to anticipate the risks, identify any significant problems early, manage the identified risks, and prevent any continuing increase in potential liabilities.

The first requirement is to ensure that the Protection of Land forms an integral part of a company's environmental management system. Secondly, local site and business management will need to be aware of where to go for guidance and expertise.

Thirdly, a system of prioritisation is necessary; scarce resources need to be allocated where they have most benefit. There are many published methods for desk top screening and some companies have developed their own in-house methods. These generally evaluate the sensitivity of the site in geological and hydrogeological terms, the proximity and nature of possible receptors, and, from an expert knowledge of the industry, the possibility of the presence of significant sources of contamination. An embryonic source-pathway-receptor approach is therefore used.

The approach taken by the regulatory community is particularly important. Wherever possible, for cases of historic contamination, industry prefers to co-operate with the regulators and to avoid adversarial positions. This recognises that the technical and economic difficulties associated with many remedial solutions requires a joint problem solving approach. Above all, we emphasise a risk management approach - not a 'do nothing' approach, nor an 'automatic clean it up' approach. This requires the development of a rigourous scientific basis for risk management which industry and, I believe, regulators, see as the only realistic way to allocate priorities and finite resources in the future.

In one of the most interesting developments last year, the Nicole network (Network for Industrially Contaminated Land in Europe), of industry and the scientific community, and the Caracas network (Concerted Action on Risk Assessment for Contaminated Sites in the European Union), of government experts and research organisations, both funded by DG12 of the European Union, produced a joint statement on research needs which is discussed later in this conference. Of significance to industry was that all parties agreed on the criteria of 'fitness for use' and 'sustainable development' in order to achieve effective and timely solutions at a viable cost to society.

REMEDIATION OF BASFORD GASWORKS USING SOIL WASHING

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Key words: soil washing, case study, pilot test, regeneration, recycling, on-site treatments, management

SUMMARY

This paper describes the first full scale application of soil washing to a major land reclamation project in the UK. Bulk samples were subjected to a series of physical and chemical tests, the results from which were used to define contractual performance targets for each class of material. The project management and technical issues arising from using site based ex-situ remediation technologies will be discussed in detail and the key process steps in the soil washing plant will be described.

RESUME

Ce document décrit la première application globale du lavage des sols à un important projet d'assèchement au Royaume-Uni. Des échantillons moyens furent soumis à une série d'essais physiques et chimiques, dont les résultats furent utilisés pour définir les cibles de performance contractuelles, pour chaque catégorie de matière. Les questions techniques et relatives à la gestion de projet, qui émanent de l'utilisation de techniques d'assainissement ex-situ sur le site, seront discutées en détail et les étapes-clés du processus de lavage des sols seront décrites.

ZUSAMMENFASSUNG

Gegenstand des Vortrages ist eine Beschreibung der ersten Anwendung des Verfahrens zur Bodenaufbereitung in einem normalen, industriellen Maßstab im Zusammenhang mit einem groß angelegten Landgewinnungs- bzw. Sanierungsprojekt in Großbritannien. Es wurden lose Bodenproben in einer Reihe von physikalischen und chemikalischen Tests untersucht. Auf der Grundlage der Ergebnisse dieser Tests wurden die vertraglich zu vereinbarenden Leistungswerte für die einzelnen Kategorien von Bodenqualitäten bzw. -materialien definiert. Die Ansätze des Projektmanagements sowie technische Fragen, die sich aus dem Einsatz von Standort gestützten Sanierungstechniken ergeben, werden in dem Vortrag detailliert erörtert, und es werden die wichtigsten Prozeßschritte in der Bodenaufbereitungsanlage beschrieben.

Contaminated Soil '98, Thomas Telford, London, 1998, 65–74

Introduction

BG plc retains over 900 ex-gasworks sites occupying approximately 2400 hectares of land. Many of these sites are occupied, or partially occupied, by live plant and equipment used for the distribution and storage of natural gas and the associated offices depots and storage areas. The remainder of the portfolio is surplus to operational requirements. Responsibility for managing the portfolio rests with BG plc Property Division (BGPD). A separate paper describes in more detail how BGPD are managing the residual environmental risks associated with an industry which provided a valuable service to residential communities and industry throughout the industrial revolution and most of this century.

BGPD are currently engaged in a major, voluntary, programme of site assessment and remediation both to reduce potential statutory liabilities and to bring sites forward for disposal/development. As one of the major practitioners of remediation in the UK at present, BGPD is constantly evaluating treatment technologies which are more sustainable and/or economically attractive than off site disposal to landfill.

The Basford site is located in north Nottingham and has been associated with the manufacture of gas since at least 1841. During its operational life, the gasworks provided considerable employment, lighting and energy to the Nottingham area as well as a range of valuable by-products for industry including coke, motor benzol, sulphuric acid and ammonium sulphate. In 1972, the manufacture of gas at Basford ceased and the site was largely cleared of above ground structures, although two gas holders, a modern Governor Compound and a number of buildings along one boundary remain.

The 7.76 hectare site had been the subject of a number of previous site investigations as part of BGPD's ongoing programme to assess its potential liabilities. Although the site conditions did not present a risk to the local community, these studies identified the need for remedial action in order to protect the underlying Sherwood Sandstone aquifer. A more detailed review of the data suggested that the soil types and contaminant concentrations might make the site amenable to treatment by soil washing. Based on this data, and taking into account BGPD's desire to introduce technology based remedial solutions, a project was initiated with the aims of i) confirming that soil washing could technically be applied to the site, ii) confirming that it could be commercially viable, and iii) applying the technology at full scale (subject to a satisfactory outcome of i and ii). Although the technical aspects are described, this paper also discusses these issues from the perspective of the planning, logistics and management of a project where the requirement to optimise utilisation of the technology had to be balanced against delivering a site remediated to the required standard.

Pilot Study

Although an analysis of soil and contaminant types based on 'typical' site investigation data can suggest that a particular remediation process might be suitable, the type and amount of data collected is usually not sufficient to provide enough confidence to

proceed immediately to full scale implementation. In the case of soil washing, the need for pilot studies is particularly relevant as there are a wide range of unit processes which could be used. Part of the reason for the pilot study on the Basford site was to select and scale the most appropriate unit processes so that an integrated plant could be constructed. A further, and very important, reason for conducting the pilot study was to allow the soil washing contractor (Linatex/Heijmans Joint Venture. LHJV) to assess the technical and financial risks and thus arrive at unit costs for the process. As the risk/reward structure of the contract was determined based on the data collected at this stage, it was considered important that the technology vendor had input into sample selection.

In order to test the hypothesis that soil washing could be undertaken on the materials from the Basford site and, importantly, produce materials suitable for reuse on the site, a treatability exercise was commissioned. Ten drum samples were taken which exhibited the range of chemical and physical properties encountered during the site investigation. These were dispatched to the LHJV's laboratories where the 'as-received' samples were visually assessed to provide a preliminary assessment of the suitability of each to treatment by standard soil washing process steps. Samples which were considered to be totally unsuitable were discarded at this stage. Representative sub-samples from each remaining sample were then analysed to determine particle size distributions and chemical properties. After combining samples with similar properties, bench scale soil washing tests were performed for each material type in order to define the optimum treatment conditions.

Based on the results of the pilot trials, chemical boundary values were defined by LHJV and subsequently used to define contractual performance targets as follows:-

i) White - material which the soil washing contractor was contracted to process 100% successfully (to a 95 percentile compliance limit) and was liable for the cost of re-processing should compliance not be attained. This category represented relatively lightly contaminated material falling above the site remediation actions values.

ii) Grey - material which the soil washing contractor was contracted to process 75% successfully (to a 95 percentile compliance limit) and was liable for the cost of any further processing to render the product chemically suitable for re-use. This category represented moderately heavily contaminated material.

iii) Black - Material which, for contractual purposes, was defined as not treatable by soil washing. However, it was agreed that attempts would be made to extend the grey/black boundary in order to maximise use of the soil washing plant and to define the true operational performance limits.

The need for pilot studies remains one of the major barriers to the introduction of many remediation technologies to the UK market. Site owners are faced with the prospect of either adopting, with a high degree of confidence, the conventional disposal to landfill approach or having to invest in further site investigation and pilot studies to prove the viability of a proposed technology. Obviously, if this additional work subsequently

shows that the technology is not suitable, the investment has been wasted. Since, at present, there is little perceived difference between off-site disposal costs and on-site treatment costs in many cases, it is difficult to justify the financial risk in embarking on a project which might have to be aborted. The scale of the pilot study is also important as larger scale tests provide more confidence. However, this also increases the financial risk and, in the case of Basford, one of the originally short listed technology vendors was rejected due to the excessively high cost and scale of the proposed pilot study. To a certain extent these are issues which have to be addressed by the technology vendors in structuring payment terms for pilot studies which, if successful would lead to full scale implementation.

Detailed Site Investigation and Site Model

The output from the pilot study was a specification for the unit processes required to treat the materials encountered on site to a standard equal to or better than the site contamination action values agreed with the Environment Agency. However, as discussed above, for technical and commercial reasons, it was necessary to specify the range of materials capable of treatment. Because of the relatively high mobilisation costs (compared to the plant required for simple off site disposal), it was felt that the site investigation data did not provide sufficient confidence in the volumes of material capable of being treated for the project to proceed. It was therefore decided that a significantly more detailed site investigation would be implemented. At face value, the cost of this was prohibitively high assuming that the only benefit was to provide confidence in the soil washing volumes. However, it must be remembered that, during the course of a typical remediation project, many hundreds of soil samples will be tested in order to characterise excavated stockpiles into waste categories or to prove that material is below the site action value and can be re-used. In this context, the approach adopted simply shifted the spend profile towards the start of the project. Obviously, there were extra-over costs associated with this approach (plant hire, staff etc.) but it is currently considered that the benefits accrued through use of this data to better plan site activities during the remediation phase and the increased confidence in project budgets outweigh the costs. A more detailed study of the costs and benefits of adopting this strategy will be undertaken at the end of the project.

The detailed investigation consisted of the excavation of trial pits on a 10m x 10m grid with appropriate sampling resulting in some 2500 chemical tests. From the physical and chemical test results, interpretation of the trial pit logs and historical information, the soil was classified, in-situ, into eleven different categories based on the processes that they were to undergo. The process streams and steps for the five 'clean' and six 'dirty' categories are shown in Figure 1. Using this information, assumptions based on previous experience and engineering judgement, a database model was constructed to generate the site excavation, processing quantities and project drawings. The processes were tiered in descending cost with the overall aim being to render material suitable for re-use with the simplest and minimum degree of processing.

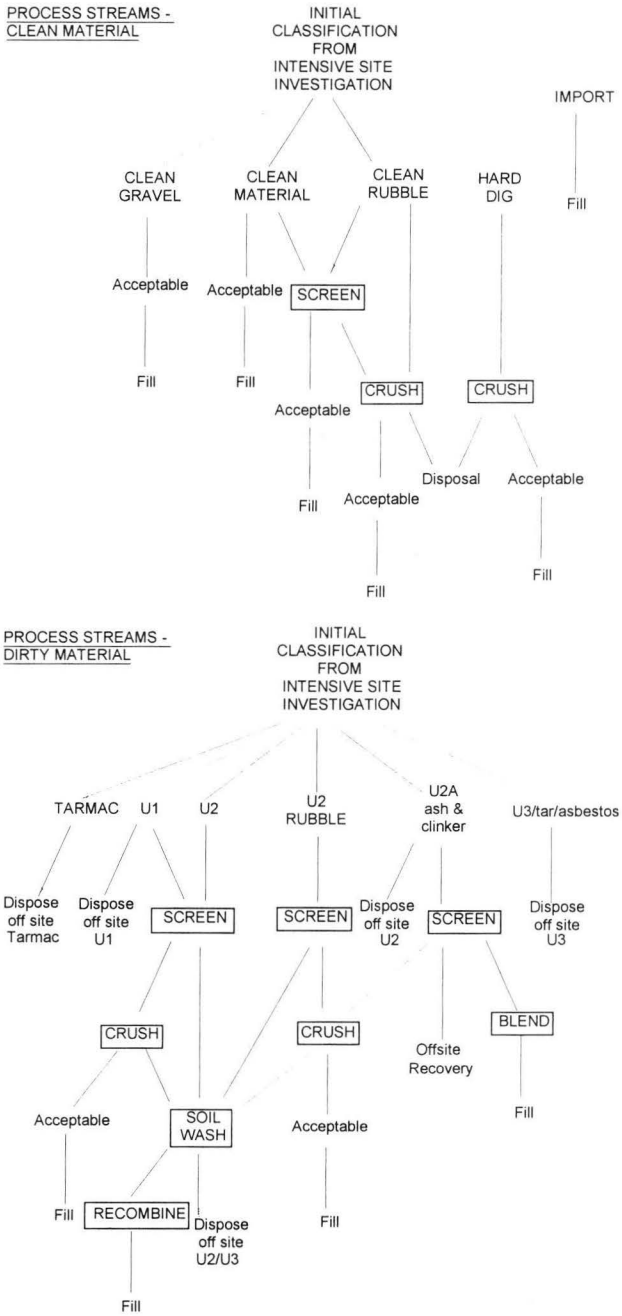

Figure 1. Categorisation of Process Streams Based on Detail Site investigation

An added benefit of producing the detailed site investigation was that the main contractors invited to tender for the project were provided with a much better conceptual model of the site than is usually the case. This allowed the successful tenderer (VHE Construction plc) to take an informed view on materials recovery (ash and coke mostly) and offer savings on the contract accordingly.

Remediation Phase

The soil washing plant was designed on the basis of the pilot study and detailed site investigation discussed above and consists of a train of process operations. The main elements of the process are shown in Figure 2 and are described in more detail below

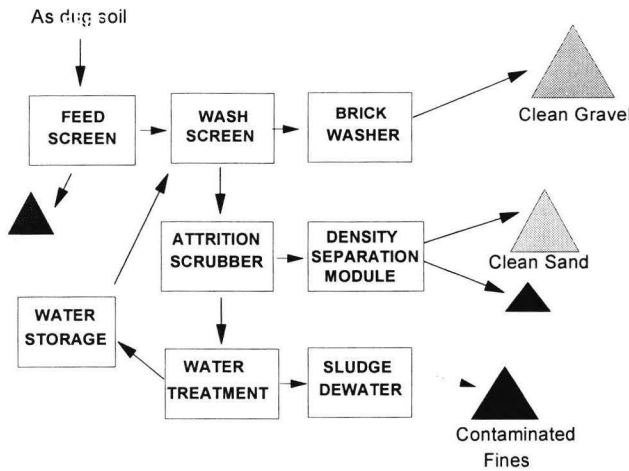

Figure 2. Main Soil Washing Process Steps

1. Excavated materials are fed into a static 150mm grizzly screen by loading shovel. Oversize is rejected, crushed and reintroduced as feed. Acceptable screened material is fed via a hopper and conveyor over a second 100mm screen. Overband magnets on the conveyor remove ferrous metals which are collected and reclaimed. The <100mm screened material is fed onto a further conveyor where a second magnet removes any remaining ferrous metal.

2. From the conveyor, the material is wetted and discharged onto a 2mm, near horizontal, vibrating screen. where it is disaggregated with high pressure water. The gravel (+2mm) fraction exits the screening and falls into a brick washer whilst the <2mm fraction passes through the screen with the water. As the gravel passes through the washer it is agitated and washed by a counter current of water. A fine screen at the

end of the washer allows the water to drain from the cleaned gravel before it is discharged into a collection bay. Material (coke, fragments of wood and plastic etc.) contained within the counter current of water discharges over a 2mm vibrating screen where it is removed for disposal. Water from the barrel washer, together with the water and <2mm material from the initial screen, is collected at the base of the module and the resulting slurry is pumped into the next stage of the process.

3. The slurry from the preceding stage is split and injected tangentially into two hydrocyclones. The hydrocyclones separate the slurry into 63 micron to 2mm 'sand' and a <63 micron slurry. The sand fraction from the two hydrocyclones passes into an attrition scrubber where a process of abrasion removes the surface contamination. Sand and the finer particles generated from this process are collected in the base of the module, where water is added before being pumped to the next stage. The slurry from the attrition scrubbers is fed into two further hydrocyclones, where the <63 micron fraction is separated from the 63 micron to 2mm sand. The slurry from the top of all of the cyclones is pumped for dewatering (stage 5, below).

4. The sand falls into a dense medium separator (DMS) where low density material (along with some fine sand) is separated from the sand fraction. Clean sand is emptied from the base of the cylinder where it is dewatered by a vibrating 63 micron screen and then discharged via a conveyor into a collection bay. The water and low density material overflowing from the DMS is discharged over an inclined fixed screen which removes the low density material and recovers the majority of the fine sand particles. Low density materials are removed by conveyor to a bay where they are collected for disposal. The water and fine sand from the inclined screen are collected in a tank and passed through a further hydrocyclone and introduced back into the process.

5. Slurry from the previous two stages containing the <63 micron fraction is collected and introduced into a 'Supaflo' high rate thickener. (Flocculants may be added at this stage if required). This process produces a sludge (up to 20-40% dry matter) which collects at the base of the tank while the water flows over a weir at the top.

6. The majority of the process water is collected in two storage tanks, the remainder is sent for additional solid removal. The stored water is supplemented by 'clean' water from the on-site water treatment plant to adjust for the losses within the clean and waste products. Additional solid removal is achieved utilising a cross flow clarifier. The water is introduced, via a conditioning tank, into a rectangular tank and passes between a series of inclined plates which accelerate the settlement of the solids. Water from this process is reused within the plant, whilst the sludge is reintroduced into the Supaflo thickener.

7. Sludge from the base of the Supaflo thickener is pumped into a conditioning tank, from where it is pumped to a continuous filter press. Additives may be introduced to enable solid particles to adhere to each other and to repel water. The resulting filter cake is collected by conveyor for disposal and forms the main waste product from the process. The belts are back-washed with the water pumped into the Supaflo thickener.

As can be seen above, soil washing comprises three main processing streams (clean gravel, clean sand and contaminated fines). Taken as unit processes, each of these streams has a limited throughput per hour. It therefore follows that, if the contaminated feed can be optimised from a physical viewpoint to ensure that each stream is taking its maximum throughput, the plant as a whole will be operating at its greatest efficiency. In addition, wild fluctuations in concentrations of the chemical contamination were found to significantly effect control of the process and the quality of the product (including the fines filter cake).

As it is rare for such an ideal and consistent blend to occur 'as dug', a high degree of flexibility was required on the part of the main contractor in targeting the excavation face to constantly supply the plant with an optimised feed at the required rate (50 tonnes/hr). By necessity this required a degree of blending and working of the feed stockpile. Economic viability would have been severely effected if the processing plant had to stand idle whilst the main contractor went prospecting for suitable contamination. The detailed ground model described above is playing a vital part in allowing the contractor to manage the site to meet this requirement. Although it has not proved to be a significant problem on the Basford site to date, it is easy to envisage a scenario where, to meet this requirement, the excavation profile becomes impossible to manage. However, it must be recognised that there is a cost associated with this activity which would not have been incurred in normal circumstances. It is therefore necessary to balance performance of the soil washing plant with the practicalities and costs associated with managing the site as a whole. These problems are eased when processing plant can accept a wide variety of feedstocks without compromising performance. Many technologies have a lower tolerance than soil washing in this respect and future research should be targeted at addressing this problem as it ultimately affects unit processing costs and hence viability.

As the soil washing process has a nominal capacity to process 50 tonnes per hour of contaminated material, the contract period is significantly longer than a comparable project involving off site disposal of all of the contaminated materials. Only one excavation team is in operation and the maximum excavation within most weeks is 5,000m^3, low by earth moving standards. Clearly, the proportionate increase in the contract overheads has an adverse effect on the economic viability of soils washing (and most other treatment processes), however, this project has demonstrated that the slower work rate has resulted on savings which, to a large extent, have recovered this additional expense. The main areas where savings are being made include:

i) *selective digging* - the detailed ground model described above allowed a 'Distribution of Materials Drawing' to be constructed which specified the depths of the interfaces between clean and contaminated material on a 10m x 10m cell basis. Combined with the relatively slow work rate dictated by the production rate of the soil washing plant and the resulting ability to provide close supervision, this approach is minimising cross contamination between layers and hence maximising direct recovery of clean material.

ii) *Ash recovery* - the contractor was able to recover ash and coke deposits for use as a smelting additive, low grade fuel and in block manufacture through simple dry screening processes. Although these activities also take place on other sites, in this instance the contractor has had more time to maximise recovery and identify suitable markets.

iii) *Import of clean fill* - partially as a result of the soil washing process and partially as a result of the relatively slow excavation rate, the contractor has not had to source a large volume of clean fill over a short time. This has brought cost savings through the ability to be more selective in the market.

iv) *Screening and crushing* - screening processes are being used to recover scrap steel, remove large fragments of wood and separate concrete and masonry from more contaminated finer material. Oversized material is then either classified as 'clean' or 'dirty' and either crushed and reused or crushed, soil washed and re-used as appropriate.

The overall economics of the project are dictated by a number of factors, the main ones being contract period, production rate of plant, unit processing costs, the efficiency of the soil washing plant (in terms of percentage recovery of 'clean' product) and its reliability. The quality of the filter cake, and in particular its moisture content, has been found to be very important because this material is designated for off site disposal on a cost per tonne basis. All of these factors are interlinked and need to be balanced to provide the most economical solution. For example, there would be little point in increasing the throughput of the plant in order to reduce the contract period if this was more than compensated for by a reduction in recovery of clean material or filter cake quality.

By the end of January 1998, some 40,000 tonnes of material had been processed through the soil washing plant with contaminant concentrations ranging from just above the site action values to the borderline of grey/black (as defined above). Only two batches of cleaned material have failed the validation tests and the quality of the product (in particular the sand fraction) has been excellent. Trial one day production runs have commenced on material contractually defined as 'black' so that the true limits of the plant can be established and its use maximised. Production rates have generally been high when the plant has been operational, however, this has been counterbalanced by reliability problems. Plant breakdowns were, perhaps, not unexpected given the unique nature of the project and modifications have been made following investigation of the more significant of these. As mentioned above, quality of the filter cake is of critical importance to the overall economics and there has been a noticeable variation in quality when processing certain types of contaminant. Again, this is constantly being monitored and improvements being made where possible.

Future Work and Conclusions

Although the project is not yet complete, the results to date have demonstrated that soil washing technology is capable of treating a wide range of soil types (made ground to natural sands) contaminated with gasworks waste. Overall economic viability compared to other approaches cannot be fully assessed until the end of the project, however, the indications to date are favourable.

This project has shown that one of the main factors governing the economic viability of soil washing is the amount and moisture content of the contaminated fines fraction and the associated disposal cost. In the extreme it is possible that a landfill operator would refuse to take such fines on the grounds of geotechnical properties alone (or at least charge a premium to take them) A method for treatment of the fines which would either render them suitable for re-use on the site or more acceptable to the landfill operator would significantly improve the economic viability of soil washing. Processes currently under consideration include solvent washing and chemical stabilisation. Pilot tests of the solvent washing process were encouraging and demonstrated that treatment targets could be attained, however, the overall economic viability is uncertain at this time.

As discussed, a major barrier to the uptake of treatment technologies is lack of confidence in the outcome, the need to fund speculative pilot studies in order to establish viability and concerns over extrapolating small scale tests to design full scale plant. Because of this, it is hoped to be able to use the soil washing plant at Basford to conduct pilot trials on large batches (hundreds of tonnes) of material from other sites. These tests will be both more economical and will provide a high degree of confidence that the material from the candidate site can be treated.

Due to the high mobilisation costs associated with most treatment processes, it is unlikely that many will be applicable to projects where there are relatively small volumes of material requiring treatment. One possible solution is to establish 'semi-mobile' processing plant which can sit on a central hub site and process materials from other sites within an economic radius for transport before moving on to another location. However, there are clearly a number of regulatory issues which need to be addressed before this can happen.

The use of a novel remediation method on this site has been very well received by a wide range of interested parties from the local residents, who have seen a key site regenerated in a manner which has minimised traffic movements, to the Environment Agency and Environmental Health Department both of whom have been supportive of the approach adopted. It is a success that BGPD hopes to repeat on other sites.

Acknowledgements

Successful remediation projects are a team effort. In this instance the project team consisted of BG plc Property Division, Parkman Group Ltd, VHE Construction plc, Linatex Heijmans Joint Venture and Davis Langdon & Everest.

EUROPEAN INDUSTRY GUIDELINE FOR RISK-BASED ASSESSMENT OF CONTAMINATED SITES

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KEYWORDS

Contaminated sites, human health risk, hydrocarbons, mineral oil, oil products, petrol hydrocarbons, refinery site, risk-assessment, risk-management, soil and groundwater contamination, soil clean-up criteria.

SUMMARY

This paper describes CONCAWE's work over the last three years to develop an overall process for Risk-Based Assessment and Management of Contaminated Oil Industry Sites Across Europe, and to produce information and tools to support this process. Also outlined are CONCAWE's current proposals to develop a range of papers addressing key issues for consideration by companies, authorities, and policy makers in establishing risk-based approaches, and developing risk-based screening levels.

Contaminated Soil '98, Thomas Telford, London, 1998, 75–81

EUROPEAN OIL INDUSTRY GUIDELINE FOR RISK-BASED ASSESSMENT OF CONTAMINATED SITES

ABOUT CONCAWE

CONCAWE is the European Downstream Oil Industry's Organisation for Health, Safety, and the Environment. Its objectives are to acquire adequate scientific, economic, technical and legal information on health, safety and environmental issues; also to improve the understanding of those issues by the Oil Industry, Authorities and Consumers.

SUMMARY

This paper describes CONCAWE's work over the last three years to develop an overall process for Risk-Based Assessment and Management of Contaminated Oil Industry Sites Across Europe, and to produce information and tools to support this process. Also outlined are CONCAWE's current proposals to develop a range of papers addressing key issues for consideration by companies, authorities, and policy makers in establishing risk-based approaches, and developing risk-based screening levels.

BACKGROUND

The potential for oil products to have an impact on soil and groundwater has long been known, but techniques for assessing and managing the risk posed by these products have only developed much more recently.

In the past, some countries have set fixed numerical criteria to decide these issues. These limits are based on generic assumptions on site conditions such as: soil type, depth to groundwater, geology and hydrogeology, and proximity to potential receptors (e.g. water well, basement, surface water body). Such an approach ignores the fact that contaminated oil industry sites vary widely in terms of complexity and the potential risk they may pose to either human health or the environment. As fixed numerical criteria are nearly always set at very low levels to ensure safety, their use leads to the clean-up of more land than may be necessary. The result is wastage of industry resources (and, ultimately, added expense to the consumer) conducting clean-up with no incremental reduction in risk to human health and the environment.

In recent years, the principles of risk-based corrective action have been applied in a number of countries in Europe and in North America where it has been developed by the American Society for Testing Materials (ASTM). This follows a flexible approach to decision-making whereby corrective action is appropriately tailored to site-specific conditions and hazards. This leads to more cost-effective solutions, and allows the greatest effort to be applied where it is most beneficial. In its broadest sense, risk assessment in relation to contaminated land can be defined, as "an evaluation of whether there is a potential for adverse effects to occur, based on factual knowledge about a site, scientific theories concerning the environmental behaviour and toxicity of the chemicals present, assumptions which have to be made where there is a lack of site-specific data, and predetermined acceptability criteria".

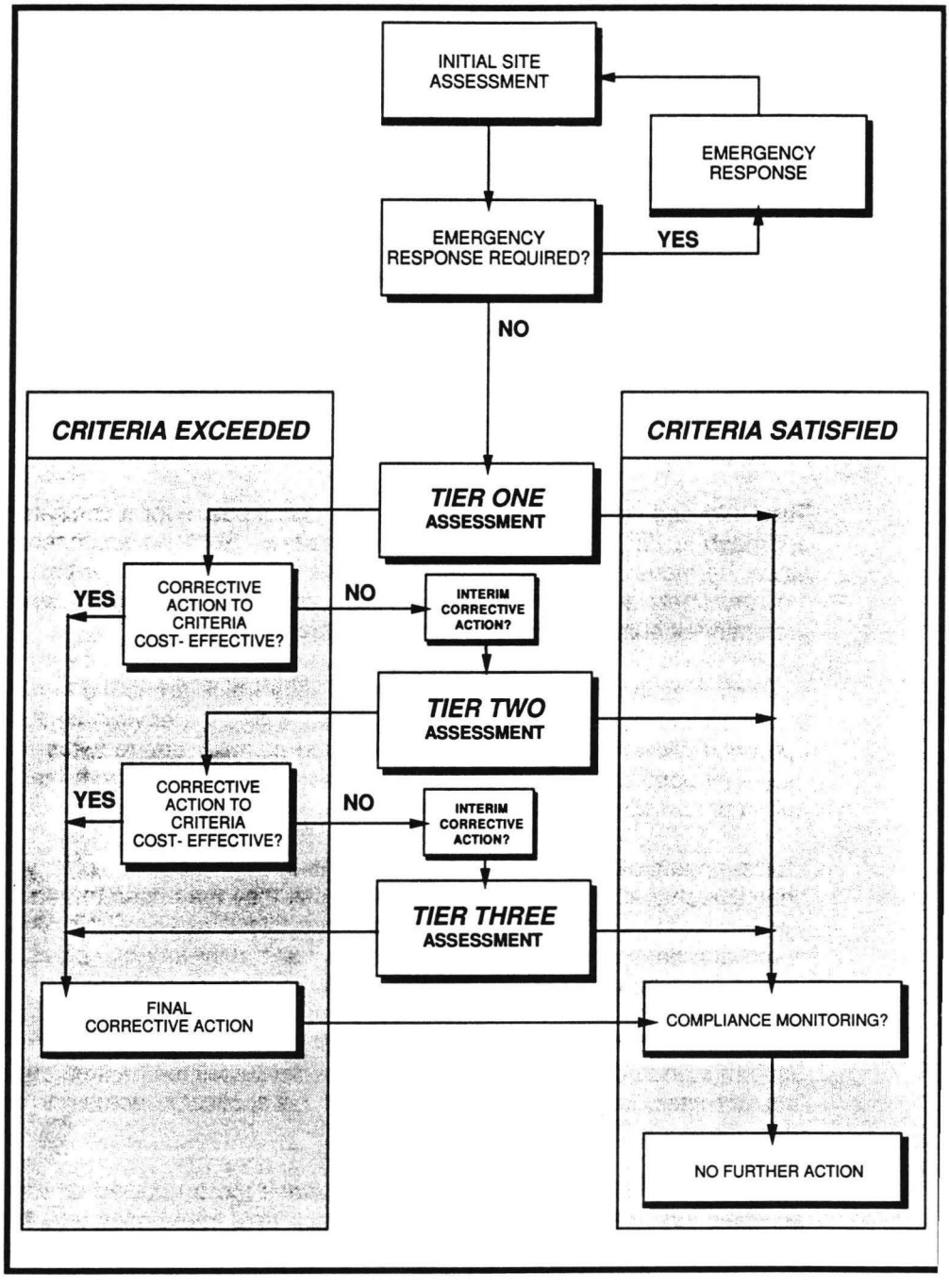
Many CONCAWE member companies have been involved with this American activity but realised that there are a number of differences between the two continents and even within them. Their wish was to develop similar techniques for Europe and they therefore established a task force to carry out this work and produce a Guideline, setting out the approach which could be adapted to the situations prevailing in the various European countries.

THE APPROACH

The CONCAWE Guideline was published in April 1997, and describes a three-tiered approach to corrective action decision-making. The Guideline is built on the premise that one begins with relatively little site data (using conservative generic assumptions), and, through additional investigation and analysis, progresses towards more site-specific knowledge and less conservatism. The result is an equal level of protection of human health and the environment throughout Tiers 1, 2 and 3.

The three-tiered approach in the Guideline is summarised schematically in Figure 1. It starts with an initial assessment of the site which involves gathering general data including potential sources of contaminants, obvious evidence of contamination, land-use, presence of potable groundwater, etc. The pathways by which contaminants could reach populations and environmental compartments at risk are also identified. This initial assessment is followed by Tier 1 in which chemical data on the degree of contamination of the site is collected and compared with Risk-Based Screening Levels (RBSL) and other relevant criteria. The RBSL's comprise a set of trigger concentrations for contaminated soil and groundwater. These figures are not intended to be soil standards or clean-up targets. If exceeded, they are simply an indication that further study is required. RBSL's are derived using conservative assumptions and contaminant migration models and, as such, are based on a generalised risk assessment. If the observed values are below these levels, then the risk will be insignificant.

Figure 1 General approach



In Tiers 2 and 3, the assessment involves refinements to the study to take into account more site-specific considerations, with the possible collection of additional data. The actual environmental compartments and populations at risk are identified, along with the possible pathways. These pathways are modelled to prepare quantitative risk estimates which can be compared with acceptability criteria. There is an option at the end of each of these Tiers to develop a corrective action programme based on remediation to the newly derived Site Specific Target Levels (SSTL). Corrective Actions could include taking no action, or instituting a long-term monitoring programme.

Although this procedure may seem complicated, it is expected to provide a consistent framework for decision-making. The outcome should be cost-effective but still result in the clean-up of those sites where it is necessary to protect man and the environment.

SUPPORTING TECHNICAL DATA, INFORMATION, AND ALGORITHMS

It was clear from the outset of the project that it would be necessary to develop data and information to support the application of the approach, for example:-

a) Single versus multiple exposure pathways
b) Importance of the Conceptual Site Model
c) Correct use of RBSL's
d) Selection of Risk Factors (e.g. 10^{-4}, 10^{-5})
e) European countries exposure assumptions
f) European / other toxicity values
g) Probabilistic Analysis
h) Use of Total Petroleum Hydrocarbon Measurement (TPH)

These issues are outlined in the published report, but in many cases require more detailed explanation, and it is planned to publish these as Technical Appendices.

DEVELOPMENT OF RISK-BASED SCREENING LEVELS (RBSL's)

During the development of the CONCAWE approach, it became clear that the use of RBSL's, and the techniques used to develop them, were particularly important issues. CONCAWE therefore embarked upon a second phase of the project to identify best practice in the development of RBSL's, which, when combined with data gathered in the first phase would allow RBSL's to be developed which were specific to the European Downstream Oil Industry, and adaptable to country-specific requirements.

The result of this work showed that in all but a few cases the algorithms, used in the North America by ASTM to develop RBCA screening levels, were best practice.

As work proceeded with the development of such screening levels, several important issues became apparent:-

1. A single screening value for each contaminant must necessarily assume the most severe exposure conditions, in order to cover all plausible situations (e.g. child, exposed throughout life to vapours, soil ingestion, water intake, dust and all other possible domestic and background levels of contaminants). Such conditions could be regarded as 'conservative multifunctionality', and can be shown to be excessively cautious and unrealistic in the vast majority of circumstances.

2. It was, therefore, necessary to develop a range of scenarios which were closer to the likely exposure, for example, domestic without gardens, recreational, ongoing industrial, etc., each posing a different level of risk to occupants and users, each generating a different set of RBSL's.

3. In each of the cases outlined in 2. above, likely exposure assumptions must be made, which may not necessarily match the situation being faced for a particular site. The user of RBSL's therefore has the potential to use these numbers out of context.

   Such situations have been experienced in the U.S. with mis-application of ASTM RBCA Screening Levels which were published only as examples. Also, some companies or authorities have taken RBSL's to represent target clean-up levels, for which they were never intended.

4. The value of the Conceptual Site Model therefore becomes apparent, in being able to eliminate consideration of pathways which do not really exist. This situation is further complicated by the fact that different countries have differing requirements. For example, some already have their own screening levels, which the Regulatory Authorities will enforce; others may require certain exposure assumptions to be used in the development of RBSL's.

5. Faced with the complications outlined above, the CONCAWE work on Technical Appendices has undergone lengthy deliberations and recycles, and whilst these are still in progress, the current thinking is outlined below.

MOST RECENT CONCAWE DEVELOPMENTS

At the time of publication of this paper, the following conclusions have been reached:

1. The most important issue in the investigation of contaminated sites is to recognise the need for Risk-Based Assessment, and subsequent Risk Management as a separate issue.

2. Risk-Based Screening Levels (RBSL's) are very useful tools for eliminating sites (or parts of sites) which truly represent no significant risk.

3. Where companies or authorities wish to use existing RBSL's, these should be chosen with the utmost care, to ensure that assumptions applicable to these RBSL's are appropriate to the site and contaminants in question.

4. The local site conditions / setting and Local or National Regulated Conditions are vital in determining how sites are to be assessed, particularly when using RBSL's.

5. Where companies or authorities wish to develop RBSL's, this process should be approached carefully, taking into consideration the range of policy, technical, and country-specific issues which exist.

To this end CONCAWE is currently preparing a range of papers which will address these issues. Recognising that Government authorities and Policy-makers in European countries will wish to exert varying degrees of influence over the approaches taken within their own domains, the purpose of the CONCAWE Guideline and papers will be to raise awareness of the key issues which should be carefully considered when formulating policy, and setting the framework within which industry will be expected to work.

Planned for publication as papers are:-

- Risk Factors and Additivity of Pathways
- Conceptual Site Model
- Probabilistic Analysis (e.g. Monte Carlo)
- Toxicity
- Compliance Points
- Total Petroleum Hydrocarbon measurement (TPH)

INTERNATIONAL STANDARDIZATION FOR SOIL QUALITY

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Key Words: Quality of the soil, soil properties, analytical methods, standardization, site investigation

SUMMARY
Increased concern about soil quality has resulted in the establishment of a Technical Committee on Soil Quality (ISO/TC 190) by the International Organisation of Standardization. The background and the reasons for standardization are discussed together with the steps which must be considered in the standardization process. The scope and structure of ISO/TC 190 is outlined with particular emphasis on the most recent developments of Subcommittee 7, Soil and Site Assessment. The importance of knowledge on possible variability of results due to different procedures of laboratory analyses is also noted.

KURZFASSUNG
Die wachsende Besorgnis um den Zustand der Böden führte zur Gründung des Technischen Komitees "Bodenbeschaffenheit" (ISO/TC 190) durch die Internationale Organisation für Normung (ISO). Die Gründe, die zu diesen Normungsarbeiten führten und die Schritte, die im Normungsprozeß zu beachten sind, werden dargestellt. Das Arbeitsgebeit und die Struktur des ISO/TC 190 werden umrissen, wobei der Schwerpunkt auf den derzeitigen Entwicklungen im Unterkomitee 7 "Boden- und Standortuntersuchung" liegt. Die Bedeutung der Kenntnis möglicher Variablitäten von Untersuchungsergebnissen, hervorgerufen durch unterschiedliche analytische Verfahren, wird ebenfalls erwähnt.

RÉSUMÉ
Par suite d'une augmentation du intérêt au sujet de la qualité du sol, L'Orgnisation Internationale de Normalisation a constitué un comité technique de la qualité du sol (ISO/TC 190). Les raisons pour le besoin de la normalisation sont discutées avec les étapes de la méthod de la normalisation qu'on doit considérer. Le domin et la structure de ISO/TC 190 est décrit avec accentuation sur les nouvelles développements de la sous-commission 7, Évaluation des sols et des sites. L'importance de la connaissance de la possibilité de la varaibilité des résultats causé par les méthodes differentes de l'anayse laboratoire est noté aussi.

Contaminated Soil '98, Thomas Telford, London, 1998, 83–91

Introduction

Throughout much of the twentieth century there has been only very limited concern about soil quality. In part this has been because, in soil, we have a resource which, whilst not infinite, has not, until recently, been considered scarce. In addition, in contrast to other key components of the environmental system such as air and water, there are few immediate public perceptions that the quality of soil is declining nor has there been a perceived threat of such decline. With respect to air there will be a public outcry if the air is polluted, unfit to breather and a potential health hazard to the population. Similarly with water, when water has proved to be potentially harmful to humans, simply unfit for consumption or unable to sustain aquatic life, there is frequently expressed public concern. This 'visual' evidence of poor air and water quality has often resulted in widescale public awareness of the nature of the problem and concern. In many countries this has resulted in 'health' driven standards for the quality of air and water, often on the basis of criteria such as 'fit to breathe' and 'fit to drink'. With soil there have been few such visual indicators; possibly the most widely observed by the public at large is soil erosion, and in some cases this has possibly resulted in an over emphasis on indicators of soil quality linked to soil erosion. A further problem faced by those concerned with soil quality is that many changes in soil often occur gradually, and it may be difficult to observe changes in soil quality even over tens of years. In addition soil is an exceedingly complex and varied material with very diverse physical, chemical and biological properties and interactions between properties and it is often difficult to select one or even a small number of properties which can serve as indicators to characterise the quality of the soil.

In recent years there has been an increased awareness of the need to establish indices of soil quality and monitor the changes in these indices. This increased awareness has arisen from a number of sources. An important source arises from the concern that our use of the land, both for agricultural and industrial activities, has resulted in contamination. A second source of concern arises from the increased awareness that we must view our current land uses in the long term and assess their sustainability. A third concern arises becaus many countries are seeking to increase the number of houses and commercial buildings, and because of this there is a need to assess the quality of the land for such expansion. In the United Kingdom, for example, the19th Report of the Royal Commission on Environmental Pollution entitled 'Sustainable Use of Soil' (1996) suggested that more emphasis should be given in future local and national development plans, to the possibility of reusing 'brownfield' sites within the current urban boundaries, rather than continuing the outward expansion into 'greenfield' sites. If this policy in the United Kingdom is to be pursued there must be criteria for assessing the quality and suitability of these brownfield sites. There is in the European Union no universal view of the criteria to be used, nor indeed in the perception of how we should address the question of soil quality. Howard (1993) reviewed the broad themes of soil quality in a European context, discussing both the different perceptions of soil quality as well as the national and international frameworks for protecting and monitoring soil quality.

Soil Quality versus soil functions– What and Why?

Whilst there is a much increased concern about the need to be able to measure and monitor soil quality, this has often been approached in a vague and unfocused manner. If progress is to be made it is essential that the question 'Soil Quality for what?' be asked and answered. Pierzynski et al. (1994) considered soil quality and the causes of reduction in quality under three broad headings:

- Reductions in soil quality because of unacceptable concentrations of contaminants;
- Reductions in soil quality that limit functions (which will probably include contamination, but also other limits to soil function such as acidification, salinisation and erosion);
- Soil as a source of contaminants (chiefly concerned with leaching and runoff losses of solute, suspended and particulate materials to other parts of the landscape).

It is therefore imperative that when assessing soil quality there is a need to consider actual and potential functions of the soil. Important functions of the soil in relation to its use by human beings include the possibility to build upon it, to produce crops, to extract groundwater and to provide raw materials. Ecological, hydrological and cultural functions will also need to be protected (Moen et al., 1986; Vegter et al., 1988). In this context a number of countries have established guidelines or laws (Anon., 1996) for soil quality and/or soil protection linked to particular functions, giving allowable levels for particular soil properties. For example, with respect to selected metals in the United Kingdom, the ICRCL Trigger Values (ICRCL, 1987) were presented for different land uses, and in The Netherland's guidelines for soil clean up were introduced in 1983 (Moen et al., 1986). In Germany the soil protection law under development will include trigger and precautionary values (Bachmann et al., 1997)

Soil Quality – which method?

Whilst indicative values or trigger concentrations were an important step forward in bringing the question of soil quality to the fore, they have only limited value if the methods to be used in determining these indicator values are not fully defined. For example when dealing with metals in soils, many of the indicators used for defining soil quality have used 'total values' for the metal under consideration, but frequently have failed to specify the method of analysis to be used in determining the 'totals'. To illustrate the importance of clearly defining the analysis used in deriving values for the total concentration of metals, Table 1 presents the results for three different, but related analytical procedures for determining the total concentrations of lead, zinc and chromium in soils (Duncan et al., 1995). Each of the methods produced different values for total concentrations of the three metals considered. Method B produced the highest values for all three metals considered, and although the differences between the results for this method and the two other analytical methods are relatively small for lead and zinc, for chromium the differences are substantial. Results from the three analyses for chromium vary by greater than 30 fold between the two methods.

Table 1: Comparison of three 'total' digestion methods for contaminated soil (Duncan et al., 1995)

	Nitric-perchloric Method A (mg/kg)	Nitric-perchloric Method B (mg/kg)	Nitric-hydrochloric (mg/kg)
Lead	355	369	301
Zinc	402	406	382
Chromium	1700	6170	172

Nitric-perchloric acids Method A (.25g soil, 8ml acid, 180°C for 1 h)
Nitric-perchloric acids Method B (.25g soil, 8ml acid, 180°C for 3 h)
Nitric-hydrochloric acids (.25g soil, 6ml acid, 120°C for 2 h)

These data illustrate the importance of the need to clearly specify the method of analysis when presenting results and attempting comparisons, but it is also important to consider analysis in terms of the purpose for which the data are to be used. For example the following analytical approaches may be relevant for different circumstances:-

- total dissolution – geochemical prospecting
- pseudo-total dissolution (aqua regia) – pollution studies
- selective extraction – determination of mobility and prediction of fate.

Alternatively the method of analysis might be determined by considering the nature of the pathways involved and their relative importance. These pathways are exceedingly diverse but might include; human consumption; influence on crop growth; and damage to buildings.

If there is to be comparability between results obtained by different laboratories and different soil media, there must be an agreement on approaches and methods. There must be standardization.

What is a standard?

It has already been stressed that the evaluation of soil quality is a complex and potentially expensive process. With regard to standardization it is important to stress that there is a difference between standard methods (such as a method for determining the dry bulk density of a soil) developed by a standards body, and standards (threshold or trigger values) set by governments or other regulatory agencies. Analytical procedures are an important component in the evaluation of soil quality, but they constitute only one step in an often complex process. The evaluation of soil quality is likely to involve at least the following steps:

Step 1 – Identification of the purpose of the study
Step 2 – Site identification and description
Step 3 – Development of a sampling protocol
Step 4 – Sampling and sample storage
Step 5 – Sample preparation and pretreatment
Step 6 – Sample analysis

Step 7 – Interpretation of the results
Step 8 – Presentation how to solve the problem or reconsideration of the initial purpose of the study.

Although most attention has been paid to analytical procedures, it is important that equal attention is given to all the other steps in the process, because failure to satisfactorily undertake anyone of these steps may invalidate the whole evaluation process.

International Standardization

With the increasing awareness, particularly in Europe, of the need to determine and monitor soil quality in a manner which allows comparisons between countries, the International Organization for Standardization (ISO) established, in 1985, a Technical Committee (TC 190) to consider the development of methodologies for establishing the quality of the soil. Progress in the developments of the scope and work programme of this Technical Committee have been outlined by Hortensius and Nortcliff (1991), Hortensius (1993) and Hortensius and Welling (1996). The Technical Committee has a subcommittee structure that emphasises the need to consider the full range of soil attributes in the assessment of soil quality, including physical, chemical and biological properties of soils. The structure of the Technical Committee also emphasises the need to address all the steps mentioned above, and not to focus simply on soil analytical methods. As a consequence there are work items concerned with the description and evaluation of soils and sites and the sampling and pretreatment of soils. The subcommittee structure developed within ISO/ TC 190 is as follows:-

SC1 –Terminology, Description and Codification
SC2 – Sampling
SC3 – Chemical Methods
SC4 – Biological Methods
SC5 – Physical Methods
SC6 – Radiological Methods (Disbanded with no standards developed)
SC7 – Soil and Site Assessment

Each of these subcommittees has a series of working groups focusing upon a particular aspect of the broad subject areas.

By the end of 1997 45 countries were involved in the work of the Technical Committee and the production of standards. Whilst there is participation from across the world, the principal participation arises from Europe, with an increasing interest from Eastern European countries. The initial production of international standards was inevitably slow, but in recent years the rate of production has increased significantly. By December 1997 there were 40 published International Standards and approximately 40 ongoing projects. Many of these standards have been simultaneously adopted as national standards. Summaries of the publication of ISO TC 190 standards are available on the World Wide Web at the following sites; ***www.bsss.bangor.ac.uk; www.iso.ch; www.din.de.***

The most recent developments in the work of the Technical Committee have been in

Subcommittee 7 which was established in 1995. SC7 is addressing the evaluation of Soil and Sites. Table 2 provides a summary of the work programme of this subcommittee:-

Table 2: The current work programme of ISO TC 190 SC7 'Soil and Site Assessment'

Working Group 1: Soil characterisation for reuse of soils and other materials **Convenor: S. Gupta, Switzerland**	**Working Group 2: Soil characterisation for the protection of water** **Convenor: J. Utermann, Germany**
Scope: The purpose of this International Standard (ISO 15176) is to provide guidance on the range of tests which may be necessary to characterise soil materials intended to be excavated and reused with, or without preliminary treatment. The following end uses are considered: agriculture, horticulture, forestry, gardens, recreational areas(e.g. parks), sports fields, restoration of damaged ecosystems, construction sites. Progress of Work: Draft International Standard	**Scope:** The purpose of this International Standard (ISO 15175) shall be to provide guidance on the principles and main methods of evaluation of soils and soil materials as a source of contamination of groundwater and their function in transporting and altering contamination. This International Standard identifies relevant monitoring strategies, methods of sampling and analysis. Progress of Work: Committee Draft
Working Group 3: Ecotoxicological characterisation of soils and soil materials **Convenor: B-M. Wilke, Germany**	**Working Group 4: Characterisation of soil with respect to human exposure.** **Convenor: L. Andersen, Denmark**
Scope: The purpose of this International Standard (ISO 15799) is to provide guidance on the selection of methods for the assessment of the ecotoxic potential of soils and soil materials (e.g. excavated and remediated soils, refills, embankments) with respect to their intended use and the maintenance of soil functions. Progress of Work: Draft International Standard	**Scope**: The purpose of this International Standard (ISO 15800) shall be to give guidance on the kind and extent of soil and site characterisation necessary for the evaluation of human exposure to substances that may cause adverse effects. The assessment may be used for classification of contaminated sites, recommendations regarding remediation, decisions regarding future use and decisions regarding the disposal/treatment of soil. Progress of Work: Working Draft

What is the expected variability when using a standard method?

An essential question to be answered in any assessment and measurement of soil quality is "What are the sources and magnitudes of variability?". It is imperative that all users of soil quality information are aware that variability in the final tabulated results of the analysis of the soil may be contributed from a variety of sources. In broad terms this might be temporal (e.g. non-systematic or random changes, regular, periodic or cyclical changes, trend changes), analytical (e.g. sampling, method, laboratory), and spatial (e.g. natural, human induced). Standardization seeks to minimise the variability associated with analytical procedures, through the development of protocols for sampling and analysis. In order to assess the likely variability due to laboratory a key element in the development of standard methods is the operation of 'ring tests' whereby soil materials are supplied to a number of laboratories who follow the preparation and analytical procedures described in the proposed method. The results of the 'ring tests' serve to assess the suitability of the method and also provide information on the likely variability arising from the method of analysis. In undertaking laboratory analysis it is necessary to be aware that repeated analysis of a soil sample for a particular constituent using the same analytical procedure will result in a population of measurement that are estimates of the level of the constituent in the sample. The differences between the central estimate (frequently the arithmetic mean) and the 'true' content is described as the *bias* of the measurement set. The distribution of the estimate is described by the *precision* of the central estimate; and if the population is normally distributed this is described by the method standard deviation. The accuracy of the individual measurements of a constituent in a soil sample is dependent on both bias (systematic errors) and precision (non-systematic errors). The bias of a set of analytical results may be considered as a combination of both the intrinsic bias of the method used (method bias) and that associated with the practices used in the particular laboratory where the method was used (experimental bias). The ring tests will provide information about both the bias and precision. This information is an essential component in the development of standard methods, because without such information it is difficult to confidently interpret the results of the analysis. In an attempt to minimise the variability due to laboratory many countries have established accreditation schemes for laboratories. Laboratories are normally accredited following an initial detailed examination of laboratory practice and results supported by a programme of regular inspections. In addition there are schemes which allow laboratories to participate in regular programmes of ring testing operating outside the programme of standard method development.

Conclusions

The evaluation of soil quality is an important activity, anticipated to grow in importance as we become more aware of the sensitivity of soils to damage and the need to consider the sustainable use of soils. In the evaluation of soil quality there must first be a clear understanding of the function of the soil – natural functions and user oriented function - which is being assessed, and the properties of the soil which may be measured to assess quality with respect to this function. Once attributes of the soil have been selected that can serve as indicators of soil quality it is essential to select standard methods of sampling and analysis for these attributes that are appropriate to this evaluation. The

ISO programme on Soil Quality is endeavouring to present a suite of standard procedures, covering all aspects of description, sampling, analysis and evaluation procedures, to assist in the assessment of soil quality. The international dimension of these procedures will allow cross border comparisons and exchange of information.

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CONTAMINATED SOIL '98

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

A FIELD STUDY TO QUANTITATE IMPORTANT CHEMICAL AND BIOLOGICAL PROCESSES IN NATURAL ATTENUATION

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Key Words: Biodegradation, bioremediation, groundwater clean-up, hydrocarbons, organic contamination, natural attenuation

SUMMARY

In order to study the geochemical and biochemical processes which contribute to Natural Attenuation of hydrocarbons in ground water systems, a subsurface residual NAPL hydrocarbon mixture was emplaced in the heterogeneous aquifer at the Columbus AFB, MS groundwater test site. Changes in aqueous and aquifer solid geochemistry and microbiology, indicative of Natural Attenuation, are being monitored as the dissolved hydrocarbon plume is formed by groundwater flow under natural hydraulic gradients. Understanding the biogeochemisrty of the aquifer will allow a better understanding of mechanisms and rates of processes which contribute to Natural Attenuation. This, hopefully, will allow us to identify easily measured indicators Natural Attenuation, and produce a scientifically validate guides for implementation.

Contaminated Soil '98, Thomas Telford, London, 1998, 95–100

Natural Attenuation (NA) is rapidly becoming the most commonly used method for remediation of groundwater contaminated with fuel hydrocarbons and solvents (Tremblay et al., 1995). In NA subsurface physical, chemical and biological processes act to decrease groundwater contaminant concentrations down gradient from a contaminant source. While there is extensive empirical evidence for natural attenuation (Mace et al., 1997; Rice et al., 1995; MacIntyre et al., 1993; Boggs et al., 1993), and protocols for implementing NA have been developed (Weidemeier et al., 1995; ASTM, 1996) the mechanisms and rates of these processes are not well understood. This ongoing study is designed to quantify these processes, and to show how they control plume development and hydrocarbon dilution, dispersion and degradation.

To simulate a subsurface release of fuel hydrocarbons a model residual jet fuel mixture was emplaced below the water table in the highly heterogeneous surface aquifer at the Columbus AFB groundwater test site. The development of a dissolved hydrocarbon plume and the changes in chemical, physical and microbial conditions within the aquifer related to development and attenuation are being monitored. From this information mechanisms and rates of the individual processes will be determined.

The objective of this project is to help solidify our understanding of the science underlying natural attenuation. Specifically, we plan to demonstrate quantitatively the Natural Attenuation process with known initial conditions, define the contribution of aerobic and anaerobic microbial processes and geological surfaces to hydrocarbon degradation, identify easily measured indicators of hydrocarbon degradation and produce a scientifically valid guide for implementing NA as a remediation technology.

The hydrocarbon source was prepared by mixing of 1188 kg of decane (75.5%), naphthalene (6.2%), p-xylene (6.1%), ethylbenzene (6.0%) toluene (6.2%) and benzene (0.05%) with 30 m^3 of clean native aquifer material. 2 kg of KBr was added as a conservative tracer. Sheet piling was driven through the surficial aquifer to an underlying clay layer to enclose an area 1 m wide by 15 long. Dewatering wells were installed around the enclosure and groundwater lowered below the source emplacement area. The aquifer materials within the enclosure were then excavated. The hydrocarbon-solid mixture was poured into the enclosure, and the trench backfilled with native material. The source zone formed was 1m thick, 1.7 m high and 15 m long approximately 10 m below the ground surface. After backfilling, the sheet pile was removed exposing the source to natural hydraulic conditions and gradients in the aquifer. The natural hydraulic gradient in the aquifer caused groundwater to flow through the source material forming a dissolved bromide and hydrocarbon plume.

The existing network of over 300 multilevel sampling wells representing 6000+ sampling points is used to collect groundwater for analysis. Additional wells are being installed as needed. Aquifer solids are collected by split spoon coring up-gradient, within and down-gradient from the plume. Groundwater and solids were sampled prior to source emplacement to measure background conditions in the aquifer. Since source emplacement, samples have been collected approximately quarterly. Groundwater is analyzed for dissolved hydrocarbons; bromide; electron acceptors including dissolved oxygen, nitrate, nitrite and sulfate; and microbial degradation reaction products including CO_2, dissolved hydrogen, methane, ferrous iron; and stable carbon isotopes. Aquifer

solids are analyzed for aerobic microbial population and degradation activity; anaerobic microbial activity and bulk and iron mineralogy.

Sampling of groundwater and aquifer solids prior to source emplacement showed that the aquifer was initially oxygenated with DO levels ranging from 0.5 to 6.9 mg/L and generally <3.5. NO_3-N ranged from 0.02-0.3 mg/L. Sulfate concentrations ranged from 0.0 to 8.6 mg/L., and dissolved Fe^{2+} ranged up to 5.0 mg/L. The natural distribution of dissolved oxygen and Fe^{2+} varied spatially throughout the site, and zones of anoxic, iron reducing conditions were observed within the aquifer. Aquifer solids are up to 1% total iron by weight, mostly as goethite with some hematite and ferrihydrite. Amorphous iron oxides were not observed.

Post emplacement sampling followed aquifer changes as the dissolved hydrocarbon plume developed and approached steady state. Bromide distribution showed that groundwater flow rates in the aquifer were on the order of 0.5 m/day, consistent with flow rates measured in previous studies at this site. The extent of the dissolved hydrocarbon plume appears to have stabilized within a few weeks of emplacement. Natural Attenuation processes are limiting the extent of the hydrocarbons plume to within 15 meters down-gradient from the source. Mono-aromatic hydrocarbons in the plume have stabilized with the leading edge at about 12 m down-gradient. The distribution of toluene, as shown in figure 1a, is typical of the distribution of mono-aromatic compounds in the plume. Naphthalene concentration was initially limited to the region nearest the source due to rapid degradation. In later samples naphthalene in the plume is seen to extended to the limit of the plume (figure 1b).

A zone of anaerobic conditions has developed immediately down gradient from the source area (figure 3). Fe^{+2} concentrations greater then 10 mg/L occur within this zone (figure 4) suggesting iron reducing conditions have developed. This increase in dissolved Fe^{+2} along the increased naphthalene stability is consistent with a shift from aerobic to anaerobic microbial processes. Aerobic microbial activity down-gradient from the source parallels the hydrocarbon distribution. Populations capable of degrading all of the hydrocarbon compounds were found in solids within the plume. In 24 hour mineralization studies aquifer solids from cores immediately in front of the leading edge of the hydrocarbon plume had the highest aerobic degradation activity. In solids from the center of the plume aerobic degraders were present but not as active. Genetic probes have shown that measurable changes in the degradative populations were associated with changing conditions within the plume.

Anaerobic microbial populations were initially present in the aquifer. Changes in populations and activity due to the introduction of the hydrocarbons are not separable from background at this point. Attempts to delineate zones of redox conditions corresponding to zones of different electron acceptor utilization based on dissolved hydrogen concentration have not been successful.

Methane concentrations in the plume are significantly above background with levels in the interior, anaerobic portion of the plume are as high as 1.6 mg/L. Carbon dioxide concentrations in the plume have increased to as high as 180 mg/L. Carbon stable isotope

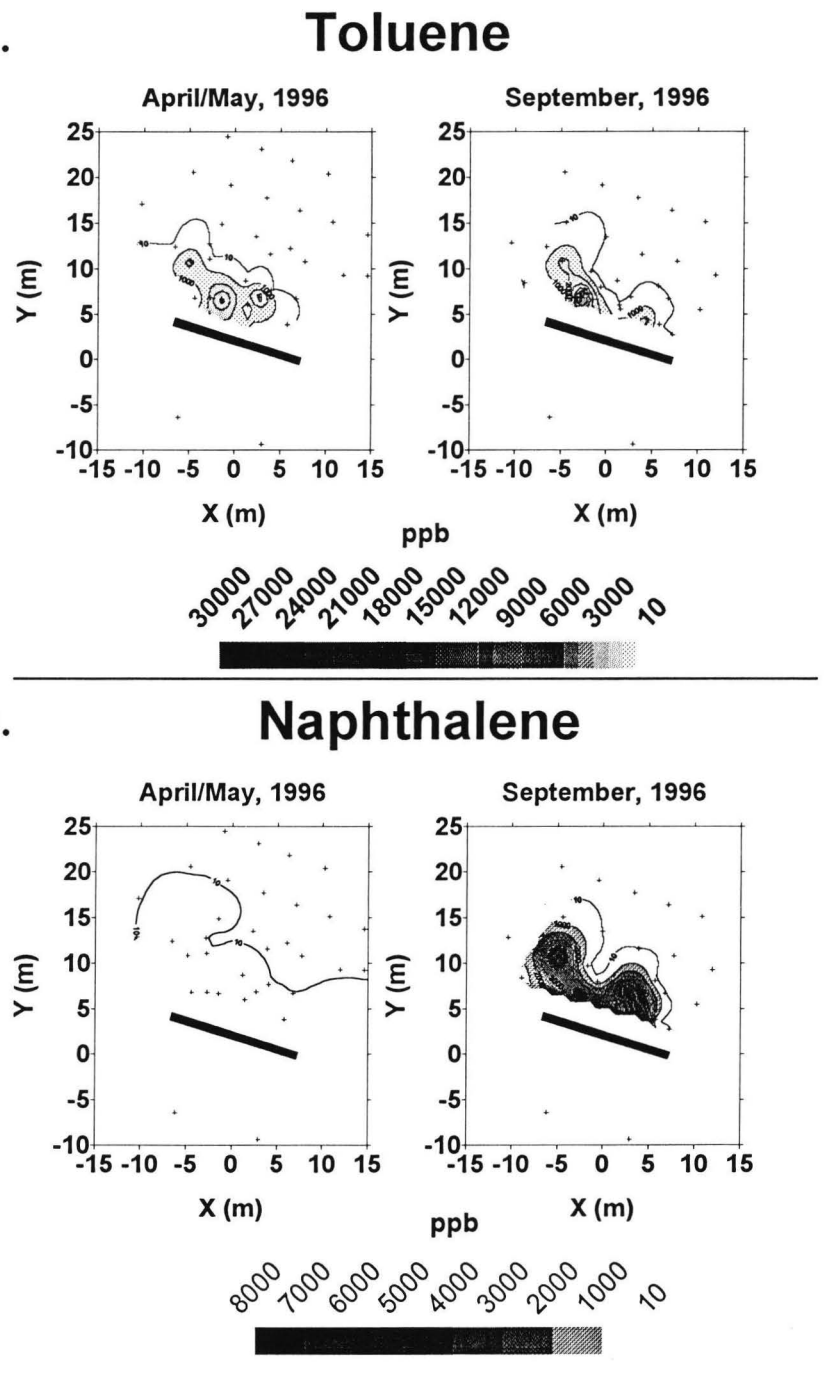
a.
Toluene
April/May, 1996
September, 1996
Y (m)
X (m)
ppb
30000
27000
24000
21000
18000
15000
12000
9000
6000
3000
10
b.
Naphthalene
April/May, 1996
September, 1996
Y (m)
X (m)
ppb
8000
7000
6000
5000
4000
3000
2000
1000
10

Figure 1

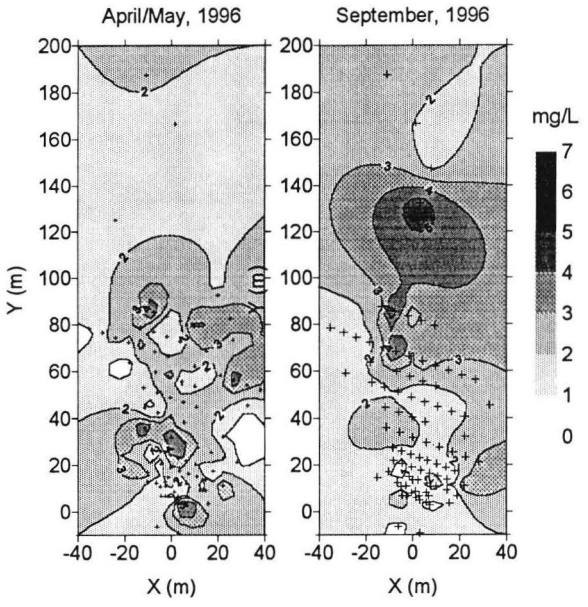

Figure 2

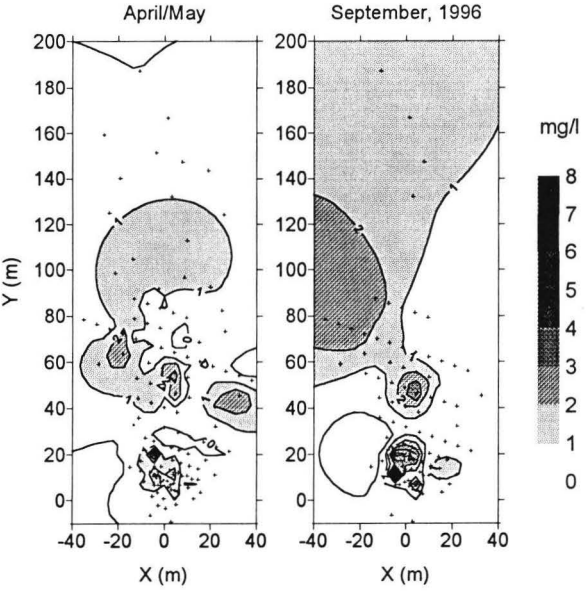

Figure 3

ratios in aqueous CO_2 and in soil gas above the plume are lighter than those measured in natural background (^{13}C = -19 to - 20) and in areas unaffected by the source. ^{13}C in the plume groundwater are as low as -21 confirming that the hydrocarbon compounds (^{13}C = -26 to-29) are being degraded.

Analysis of plume movement and aquifer conditions demonstrate that Natural Attenuation is limiting the extent of the hydrocarbon plume. Geochemical and microbial indicators show that initially aerobic processes controlled the fate of the compounds. The system is beginning to develop an anaerobic zone in the center of the plume and anaerobic microbial processes are becoming more important. Changes in plume composition, such as greater naphthalene concentration, confirm a shift from aerobic to anaerobic microbial processes is occurring. Increased levels of Fe^{+2} along with low dissolved oxygen suggest that the plume has become iron reducing. This is not confirmed by dissolved hydrogen concentrations, possibly because of the heterogeneous nature of the sediments which make up the aquifer.

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COMPARISON OF FIELD AND LABORATORY METHODS FOR DETERMINATION OF POTENTIAL FOR NATURAL ATTENUATION IN A LANDFILL LEACHATE PLUME (GRINDSTED, DENMARK)

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Key words: Natural attenuation, aromatic hydrocarbons, field injection experiment, *in situ* microcosms, laboratory batch experiments

SUMMARY
An anaerobic field injection experiment was performed in a landfill leachate plume. The field injection lasted for 195 days, and the injected cloud was monitored over a period of 924 days as it travelled through a redox environment dominated by iron reduction. Anaerobic degradation was observed for toluene, *o*-xylene, naphthalene, while benzene was not degraded in the aquifer. No conclusions could be made for ethylbenzene and *m/p*-xylene due to varying background concentrations. The experimental periods were up to 220 days in the ISM experiments and 537 days in the LB experiments. Only toluene was degraded in the ISM, while also *o*- and *m/p*-xylene was degraded in the LB. Benzene, ethylbenzene and naphthalene were not degraded in either the ISM or the LB. generally a good accordance between the different experimental approaches was obtained.

Contaminated Soil '98, Thomas Telford, London, 1998, 101–108

INTRODUCTION

The xenobiotic compounds benzene, toluene, ethylbenzene, and xylenes (BTEX) are often found in groundwater affected by landfill leachate (Christensen *et al.*, 1994). These compounds constitute a serious problem to groundwater pollution due to their potential health risk. Millions of old landfills exist through out the world, and traditional remedial action (excavation, pump- and treat) is not realistic at all these sites. This makes natural attenuation or intrinsic remediation very interesting as a remediation technology for landfill leachate plumes. The basic concept behind intrinsic remediation is to allow naturally occurring biological or chemical processes to degrade contaminants. Use of this approach will require an assessment of the potential for degradation and of the factors that govern the degradation capacity of the aquifer.

The purpose of this study was to provide field evidence on natural attenuation, (transport, dilution, sorption, degradation and degradation rates) of different xenobiotic compounds in an anaerobic leachate plume by performing a natural gradient injection experiment. Also it was the purpose to compare the degradation of xenobiotic compounds in more simple experimental systems, *in situ* microcosm experiments and laboratory batch experiments carried out in parallel to the injection experiment with that obtained in the natural gradient injection experiment. The experiments involved 18 xenobiotic compounds, however, only the results for the seven aromatic hydrocarbons will be presented here.

In 1992 and 1993 the distribution of redox sensitive parameters and organic compounds was mapped along two 300 m long transects downgradient of the Grindsted landfill, Denmark (Bjerg *et al.*, 1995; Rügge *et al.*, 1995). The study was performed downgradient of an area where mainly household waste had been landfilled (Kjeldsen *et al.* 1998a,b). At the border of the landfill, more than 15 different xenobiotic compounds were identified in concentration levels of 1-1550 µg/l. At a distance of 30-60 m most of the compounds were no longer detectable (<1-5 µg/l). Dilution and sorption could not account for the observed fate of the compounds, and it was proposed that significant degradation was occurring within the anaerobic plume under methanogenic/sulfate-reducing or iron-reducing conditions. On the basis of these investigations, an anaerobic field injection experiment was designed in order to establish direct proof of the proposed degradation.

MATERIALS AND METHODS

In order to cover a range of mobilities as well as expected potentials for biotic and abiotic degradation, some compounds already present in the leachate plume and some compounds supposed to be present in landfill waste were chosen for the study. A total of 18 different xenobiotic compounds were selected as model compounds (Rügge *et al.*, 1998). An anaerobic stock solution of the 18 different xenobiotic compounds (seven aromatic hydrocarbons: benzene, toluene, ethylbenzene, *o*-, *m*-, *p*-xylene, naphthalene; four chlorinated aliphatic hydrocarbons; five nitrobenzenesand two pesticides was injected along with bromide as tracer into five injection wells, installed 15 m downgradient of the landfill. The amount of water injected in the natural gradient experiment was approximately 5% of the groundwater flux passing the injection wells, yielding approximate concentrations of 75-330 µg/l of the xenobiotic compounds and of bromide of 100 mg/l immediately downgradient of the injection wells.

The migration of the compounds was monitored in a dense sampling network consisting of a total of 140 multilevel samplers (1030 sampling points), Fig. 1. Over a period of 924 days samples were collected from approximately 70 discrete sampling points in the central part of the cloud for the determination of breakthrough curves (BTCs). From the BTCs degradation and sorption could be determined. After end of the injection, seven cloud snapshots were established covering approximately 400-700 sampling points each time. From the snapshot, moment analysis provided an evaluation of the mass loss of solute in the system and the spatial distribution of the cloud in the aquifer. In total more than 20,000 groundwater samples were collected, for analysis of bromide, aromatic and chlorinated aliphatic compounds, ^{14}C-benzene, $^{14}CO_2$, ^{14}C-total activity, nitroaromatic compounds, anilines, pesticides, and redox sensitive compounds (Rügge *et al.*, 1998a,b).

In parallel to the injection experiment, *in situ* microcosms (ISMs) were installed at five locations downgradient of the landfill, Fig. 1 (see Nielsen *et al.*, 1996 for description of this technique). Also laboratory batch experiments (LBs) were conducted with sediment and groundwater from the corresponding locations, Fig.1. The experimental periods of the in ISMs and the LBs were up to 220 and 537 days, respectively. Both systems involved the same mixture of the 18 compounds (Bjerg *et al.*, 1998).

The redox conditions in the studied area of the plume were determined by analysis of water soluble redox sensitive compounds sampled every 6-8 weeks during the experimental period and by groundwater and sediment characterizations combined with microbial assays conducted on sediment and groundwater sampled 800 days after start of the injection (Rügge *et al.*, 1998a).

RESULTS AND DISCUSSION

Redox conditions

In the studied part of the aquifer, iron reduction was the dominating redox process, but also methanogenesis and sulfate reduction occurred close to the injection wells. Throughout the plume, a redox gradient towards less reduced conditions was observed, and in a distance of approximately 45 m from the landfill, methanogenesis and sulfate reduction were no longer detected. The difficulties in determining redox conditions in low-activity matured plumes was clearly demonstrated, and because of this complexity no simple methods can be used for characterization of redox conditions in strongly anaerobic leachate plumes (Rügge *et al.*, 1998a).

Degradation

I the injection experiment, degradation was observed as a complete mass removal of toluene within the most reduced part of the aquifer where iron reduction, sulfate reduction and methanogenesis occurred. Partial degradation was observed for *o*-xylene and naphthalene. The degradation of *o*-xylene was not initiated before the cloud had reached the less reduced part of the aquifer, while naphthalene was degraded over the entire part of the aquifer studied. Examples of BTCs at 20 m and 35 m are given in Fig. 2. Benzene was not degradable within the experimental period of 924 days. Due to highly varying background concentrations, it was not possible to determine whether any degradation of the three compounds ethylbenzene and *m/p*-xylene occurred.

The experimental periods were up to 220 days in the ISM experiments and 537 days in

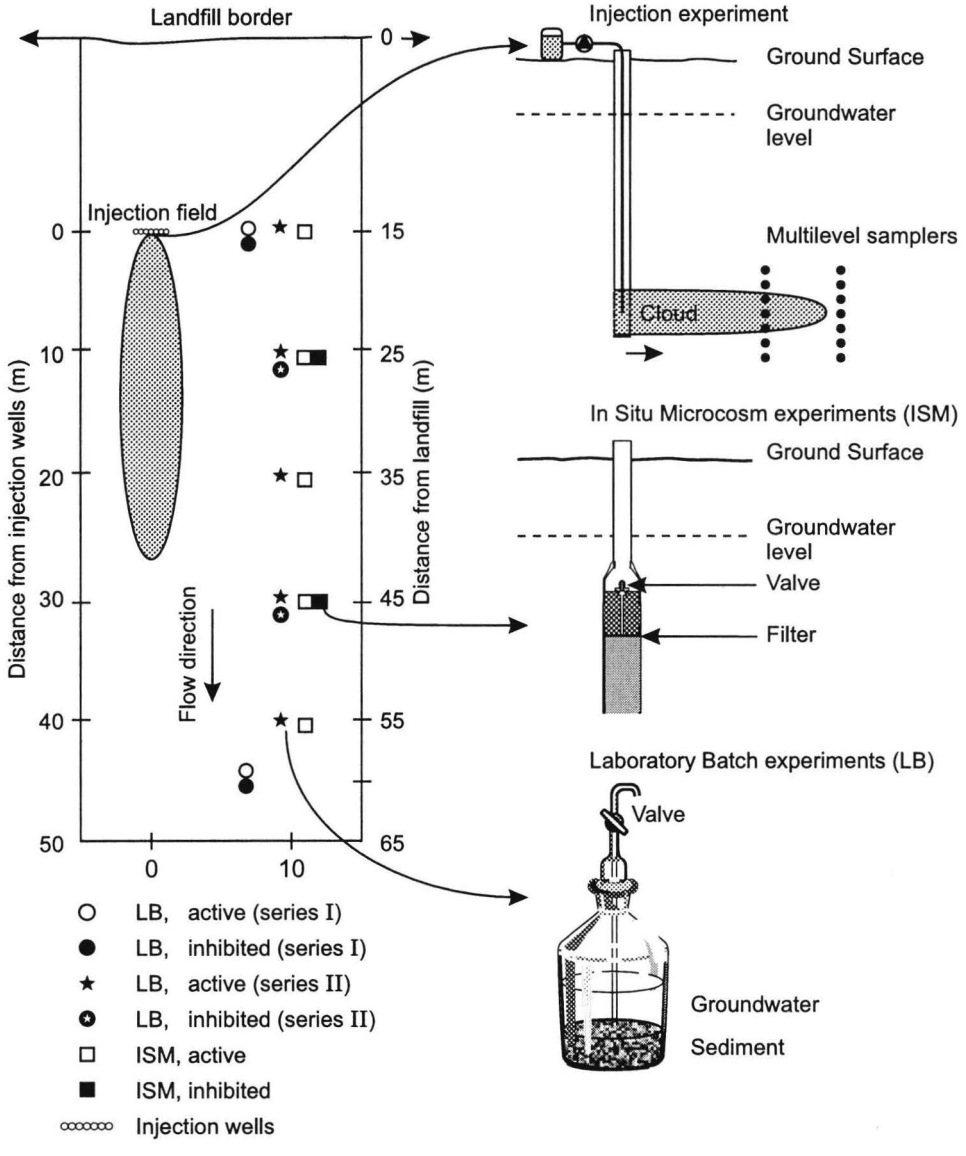

Figure 1. The location of the injection experiment, the *in situ* microcosm experiments, and the laboratory batch experiments within the experimental area downgradient of the landfill.

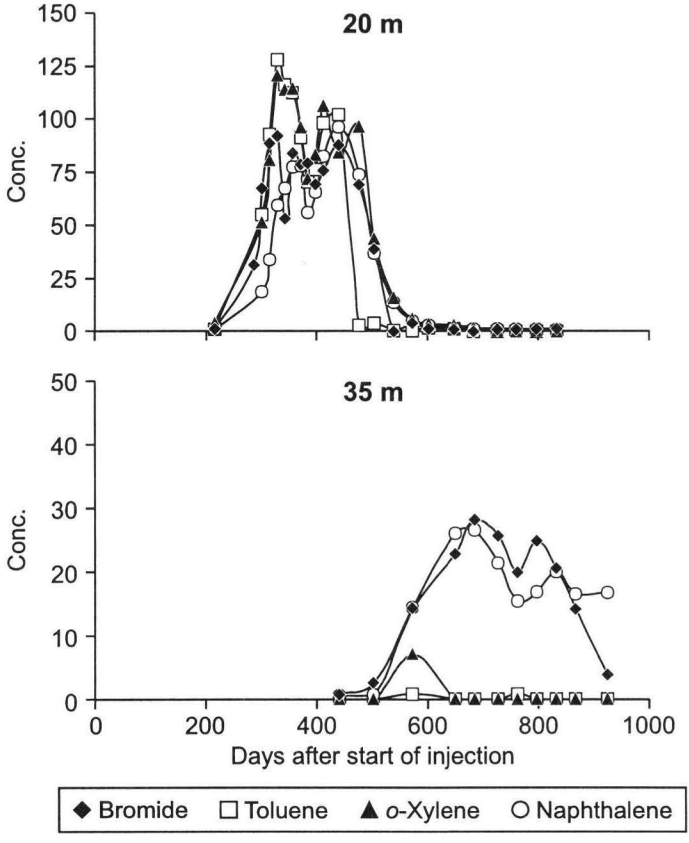

Figure 2. Examples of breakthrough curves for bromide, toluene, *o*-xylene and naphthalene at 20 m and 35 m distance from the injection wells. Concentration of bromide in mg/l and of the xenobiotic compounds in µg/l.

the LB experiments. Only toluene was degraded in the ISM, while also *o*- and *m/p*-xylene was degraded in the LB. Benzene, ethylbenzene and naphthalene were not degraded in either the ISM or the LB. Examples of fate curves are given in Fig. 3.

Comparison between the field injection experiment, laboratory batch experiments and *in situ* microcosms

In general a good accordance was observed between the results obtained in the injection experiment, the ISMs, and the LBs, however, a few differences appeared. These differences were mainly due to the different experimental periods of 924 days in the injection experiment, and up to 210 and 537 days in the ISMs and LBs, respectively. However, also the difference in a static and a flow system influenced the results. This comparison indicated that the ISM is a good method for studying degradation in the field for compounds without too long lag periods. LBs are also a useful and cost-saving approach for studying degradation. The batch set-up allow for very long experimental periods. Therefore the LBs are usable for mixtures of compounds with both shorter and longer lag periods as well as for compounds with varying degradation rates. The results on degradation, however, have been obtained for rather simple compounds, and it is not known, how well the batch experiments mimic the field situation for more complex compounds.

FINAL REMARKS

The previous plume observation downgradient the Grindsted Landfill indicated a potential for degradation of xenobiotic compounds within 60 m distance from the landfill. Generally, this was confirmed by the results from the three different experimental systems. However, benzene degradation was not confirmed by any of the experiments. In the literature, varying results on degradability of the xenobiotic compounds studied in landfill leachate are presented (Acton & Barker, 1992; Johnston *et al.*, 1996; Nielsen *et al.*, 1995). In general, the results obtained by the three approaches (injection experiment, ISMs and LBs) were in good accordance with earlier presented field and laboratory experiments and with existing landfill plume observations (Rügge *et al.*, 1995). The experiments showed, that not all aromatic hydrocarbons are easily degradable under anaerobic conditions. Furthermore, some of the other xenobiotic compounds included in the experiment formed hazardous degradation products. This means that, although this project is an important step in understanding the natural attenuation processes in leachate plumes, the fate of degradation products and the change in toxicity should be scientifically addressed before natural attenuation is considered a viable alternative to other remediation technologies.

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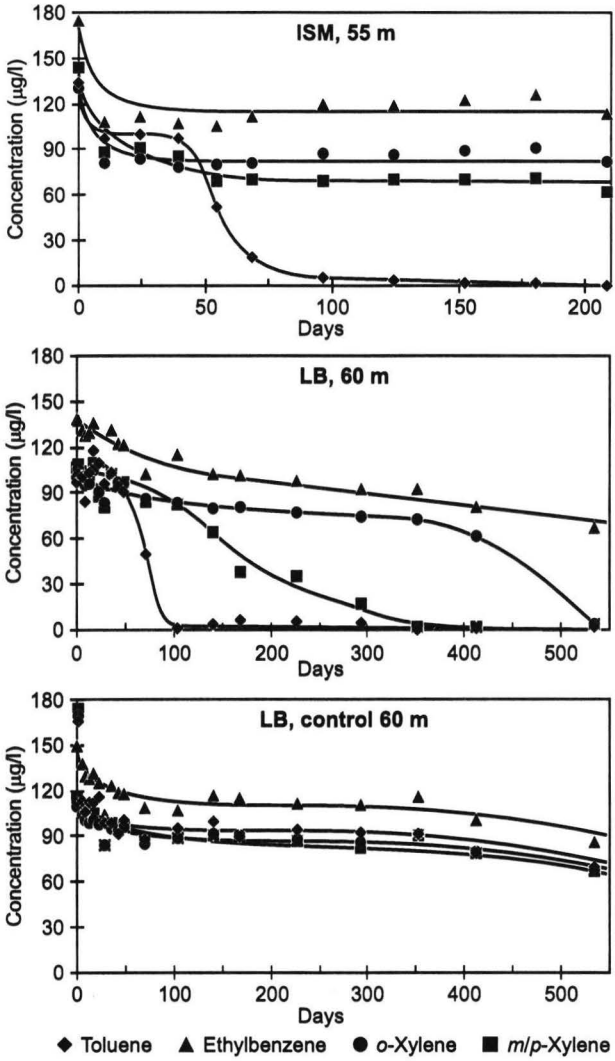

Figure 3. Concentrations of toluene, ethylbenzene, *o*-xylene, and *m/p*-xylene over time in the *in situ* microcosm experiments at 55 m distance from the landfill and in laboratory batch experiments for active and a biologically inhibited control experiments representing 60 m distance from the landfill

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INTRINSIC AND ENHANCED BIOREMEDIATION IN AQUIFERS CONTAMINATED WITH CHLORINATED AND AROMATIC HYDROCARBONS IN THE NETHERLANDS

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Key-words: Groundwater, natural attenuation, in situ bioremediation, microbial degradation, barriers, chlorinated hydrocarbons, trichloroethylene, aromatic hydrocarbons, benzene, pesticides, HCH HexaChlorcycloHexane, risks, guidelines

SUMMARY

The feasibility of intrinsic and enhanced bioremediation approaches for 16 contaminated sites in the Netherlands are discussed. At at least five out of 10 chlorinated solvent sites, natural attenuation can be used as one of the tools to prevent further dispersion of the plume. At two sites stimulation of the intrinsic dechlorination processes in a bioactived zone is required, and pilot field tests are currently under way. For three sulphate-reducing/methanogenic aquifers contaminated with aromatic compounds, microcosm studies demonstrated that natural anaerobic degradation of the risk-determining benzene does not to occur spontaneously. Benzene biodegradation could be initiated by feeding small amounts of oxygen (in all samples) or nitrate (only in one sample), and these techniques are currently tested in field-pilot studies. Redox-microbiological characterisation of two locations contaminated with hexachlorocyclohexanes indicated significant intrinsic biodegradation of HCH's in methanogenic/sulphate-reducing parts of the contaminant plumes, and of the HCH-degradation products chlorophenol and benzene under sulphate/iron reducing conditons. Biostimulated zone's remain required to complete the degradation of HCH and the degradation product monochlorobenzene. Risk-based guideline's for assessing the feasibility of natural attenuation approaches for various contaminant situations are currently under development, making use of already existing protocols (USA) and taking European and National specific conditions, knowledge and regulatory constraints into account.

Contaminated Soil '98, Thomas Telford, London, 1998, 109–112

Introduction

The ideas concerning best approaches for remedation of polluted soil and groundwater are rapidly changing. A few years ago many engineers and regulators considered contaminated aquifers as biologically inactive systems which could only be remediated by very drastic and expensive methods like soil vapour extraction or large scale pump-and-treat. Nowadays, one has become aware that the natural microbial population in soil and groundwater react actively when confronted with pollution, and thus offer new and better ways to protect groundwater resources at acceptable costs.

Often, natural biodegradation processes can convert large amounts of contaminants without any external stimulus. Sometimes, the natural processes can completely degrade or immobilise pollutants during their down-gradient transport. When sufficient time and space is available, an intrinsic remediation approach can in principal be completely protective for man and surrounding ecosystems. At other sites, the natural biodegradation processes need to be enhanced in order to obtain a sufficient risk reduction and groundwater protection. Such a stimulation can be performed in a bioactivated zone or bioscreen. In such a zone, the autochtonous bacteria are supplied with the appropriate electron donors, acceptors or nutrients. At some sites, the microbial population is not yet fully adapted to the most optimal biodegradation process. In such a case bioaugmentation of the bioscreen may be a solution. Intrinsic remediation, when necessary combined with bioscreens, is becoming the new approach to deal with large and complex contaminated sites.

Natural and enhanced attenuation as a risk based solution for contaminated soil and aquifers is currently being investigated at various sites in the Netherlands. A number of 16 cases investigated by TNO will be discussed below.

Chlorinated solvents

At the Rademarkt site (Groningen, The Netherlands) contaminated with perchloroethylene (PCE) and trichlorethylene (TCE), mixed redox conditions control the intrinsic biodegradation processes. In a methanogenic/sulfate reducing zone a complete reductive dechlorination reaction via vinylchloride to ethene and ethane occurs. However, the natural transformation rates of vinylchloride observed in the field (and in the laboratory) are too slow to prevent migration of this hazardous compound to areas to be protected. The low amounts of DOC (< 10 mg/l) indicate a lack of sufficient amounts of electon donor naturally present. Laboratory experiments identified a special mixture of electron-donors to be the most suitable cost-effective product to enhance the in situ reductive dechlorination. An in situ pilot test with an anaerobic activated zone designed for complete reductive dechlorination is planned this fall. In another flow direction in the field, the redox condition changes from methanogenic/sulfate reducing to oxic conditions. In the reduced part, PCE and TCE are transformed to cis-1,2-dichloroethylene (DCE) and vinylchloride (VC), which both disappear after entering the oxic zone. Probably, these compounds are removed by intrinsic oxidation. Hence, in this flow direction a complete sequential degradation of the chlorinated compounds is achieved.

At another PCE/TCE site in Maassluis, the contaminated aquifer contains high concentrations of organic carbon (up to 700 mg/l DOC). Here, complete reductive dechlorination is observed. Most likely, this is a result of the high amounts of intrinsic electron-donor and a well adapted autochtonous microbial population.

The results of the characterisation of redox conditions and intrinsic biodegradation at 10 chlorinated solvent sites are as follows. For at least five of these sites, intrinsic bioremediation is an important part in an approach to effectively control the risks. At at least two sites, in-situ biodegradation needs to be stimulated in in-situ activated zones to protect down stream area's.

Intrinsic chlorinated solvent remediation is further investigated by testing electron donors and measuring in-situ hydrogen pressures in the field and in laboratory microcoms. Thus a further insight into mechanisms involved will be obtained.

At present new technologies are being developed by TNO for application in bioscreens and remediating chlorinated solvent hot-spots and contaminated soils and subsurface layers with low permeability. Combination of electroreclamation techniques and biological methods appear to bring new solutions in the near future.

Aromatic and oil-related hydrocarbons

Aromatic compounds are often the risk controlling compounds at oil and gas production sites, and at sites of coating and nutrition industries. At three sites in the north part of the Netherlands, deep anaerobic aquifers contaminated with Benzene, Toluene, Ethylbenzene or Xylenes (BTEX) have been investigated. Under the existing sulfate-reducing conditions, the intrinsic biodegradation of toluene and ethylbenzene could be demonstrated in the field and in microcosm studies. Benzene biodegradation could not be evidenced with the field data. Laboratory microcosm studies with five different sediment samples were performed. For each sample a series of comparable triplicate microcosms were incubated; in total about 300 microcosms were used. The results demonstrate thus far (200 days of incubation) that spontaneous intrinsic anaerobic benzene biodegradation does not occur in these sediment and groundwater samples.

Microcosm method development studies indicated that special care is required to prevent artefacts: "apparent intrinsic anaerobic" benzene biodegradation could be demonstrated to originate from low (often not measurable) amounts of oxygen introduced into the systems, when inappropriate materials and techniques were used.

Microcoms were also used to investigate possibilities to stimulate biodegradation of benzene and TEX compounds. Especially, addition of nitrate and low amounts of oxygen to the anaerobic samples was studied. In one out of the five series of sediment-microcosms, nitrate-reducing benzene biodegradation appeared to occur after lag-times greater than 80 days. In addition, anaerobic benzene degradation could be initiated in all samples by spiking low amounts of oxygen. Further investigations are underway to elucidate mechanisms and quantify remediation process parameters. The results are used for designing pilot demonstration tests to be performed this spring/summer.

At an oil refinery site in the Rotterdam Harbour area, an aerobic reactive-trench bioscreen is tested for managing a plume of the dissolved fraction of a mineral oil contamination (80% of the compounds belong to the C6 - C12 fraction). Bench scale experiments are currently performed to establish i) optimal grain-size and packing density for the porous media used in the trench, ii) optimal oxygen supply rates to sufficiently initiate aliphatic hydrocarbon biodegradation and to minimise clogging with iron(III)oxides.

Chlorinated pesticides

Hexachlorocyclohexane (HCH) isomers are important pollutants introduced by the production of lindane (gamma HCH). At two sites, anaerobic intrinsic biodegradation of HCH and corresponding degradation-intermediates (benzene and monochlorobenzene) is currently being investigated. At one site, natural biodegradation processes appear to completely degrade all compounds except the monochlorobenzene; possibly some biostimulation may be required at the downstream end of the plume. At the other site, interception of the HCH/Chlorobenzene/benzene plume is required. A bioactivated zone as an alternative to conventional large scale pump-and-treat is currently being investigated. At present, laboratory process research aimed at developing a combination of anaerobic-microaerophilic in-situ stimulation in such a bioactivated zone is being performed. The results indicate good prospects of such an approach, and further development and pilot scale demonstration is being planned.

Natural attenuation guidelines

Dutch (NOBIS) and Nicole-supported guidelines for assessing the feasibility of natural attenuation approaches for various contaminant situations are currently under development, making use of already existing protocols (USA) and taking Dutch/European specific conditions, knowledge and regulatory constraints into account. These guidelines are to become tiered decision tools. In the first steps a minimum of data is required for a first feasibility screaning, thus saving costs. At higher tiers, data-requirements are designed to address natural degradation under various redox-situations (including sequential redox conditions) that often occur in European sedimentary regions.

Conclusion

Intrinisic and enhanced in-situ bioremediation approaches become more and more accepted as appropriate cost-effective solutions for aquifers and soils contaminated with organic chemicals. These techniques still need to be further developed and demonstrated and could also be expanded to control and remediate mixtures of organic and inorganic (heavy metal) pollutants.

ACKNOWLEDGEMENTS

The various projects discussed are partially funded by industrial companies, regional Dutch government agencies, two Dutch Ministries (of Economic Affairs and of Public Health, Housing, and Environment), NOVEM, NOBIS, NICOLE, and performed in co-operation with consultancy and contractor companies, and universities.

ANALYSIS, BEHAVIOUR AND FATE OF A LIGNITE PYROLYSIS WASTEWATER DEPOSIT

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Key words: Phenols, in-situ bioremediation, humic substances, flocculation, sorption, PAH, sediments

SUMMARY

For decades, effluent from the lignite pyrolysis plants formerly operated in Central Germany has contaminated the region's groundwater and surface water. In order to develop remediation strategies, the case-study of a pyrolysis wastewater deposit (a lake with a surface area of 9 ha and a volume of 2,000,000 m^3 was used to investigate the complex characterisation of the deposit, as well as the fundamental chemical and biological reactions of pyrolysis water altered by storage.The group of anthropogenic humic substances (AHS) was perceived as determining the chemical behaviour and the biological effects. In order to forecast the activation of the self-cleaning of the lake after AHS removal by flocculation with ferrous chloride, *in situ* enclosure experiments were performed. The results of pollutant degradation help predict the success of treating the entire lake and provide initial conclusions concerning the decontamination of polluted groundwater.

RÉSUMÉ

Les eaux résiduaires provenant des installations de pyrolyse du lignite exploitées en Allemagne centrale ont pollué des décennies durant les nappes phréatiques et les eaux de surface de la région. Pour élaborer des concepts de dépollution, on s'est appuyé sur l'étude d'un dépôt d'eau de pyrolyse (un lac d'une surface de 9 ha et d'un volume de 2 millions de m^3), afin de procéder à la caractérisation complexe du dépôt et d'analyser les réactions chimiques et biologiques fondamentales d'une eau de pyrolyse vieillie du fait de la mise en dépôt. Le groupe des substances humiques anthropogènes (SHA) a été reconnu déterminant pour le comportement chimique et les effets sur la biologie. Des expériences ont été pratiquées en milieu clos in situ pour prévoir l'activation de l'autonettoyage biologique du lac après enlèvement des SHA par floculation avec le chlorure ferrique. Les résultats de la décomposition des substances polluantes permettent de présager du succès du traitement du lac dans son ensemble et de tirer les premières conclusions sur la décontamination de la nappe phréatique.

KURZFASSUNG

Abwässer der ehemals im mitteldeutschen Raum betriebenen Braunkohlenpyrolyse- Anlagen verunreinigten über Jahrzehnte die Grund- und Oberflächenwässer der Region. Zum Erarbeiten von Sanierungskonzepten wurde die Fallstudie einer Pyrolysewasserdeponie (einem See von 9 ha Oberfläche und 2 Millionen m^3 Volumen) genutzt, um die komplexe Charakterisierung der Deponie vorzunehmen sowie die grundlegenden chemischen und biologischen Reaktionen zu untersuchen. Die Gruppe der anthropogen entstandenen Huminsubstanzen (AHS) wurde als bestimmend für das chemische Verhalten und die Auswirkungen auf die Biologie erkannt. Zur Prognose der Aktivierung der biologischen Selbstreinigung des Sees nach einer AHS-Entfernung durch Flockung mit Eisen(III)-chlorid wurden *in situ*- Enclosure-Experimente durchgeführt. Die Ergebnisse des Schadstoffabbaus lassen eine Aussage über den Erfolg der Behandlung des gesamten Sees zu und gestatten erste Rückschlüsse auf die Dekontamination von kontaminiertem Grundwasser.

Contaminated Soil '98, Thomas Telford, London, 1998, 113–121

1. Introduction

History of the deposit

For the lack of a better solution, highly concentrated effluent from lignite pyrolysis began to be deposited in the 1930s in disused opencast mines (such as from the plant at Deuben, near the town of Zeitz in Saxony-Anhalt). Whereas at other locations this wastewater drained away underground, in one case geological conditions resulted in it forming a lake (now known as Vollert Süd or Schwel-Vollert, and commonly referred to as "phenol lake"). In conjunction with the pressing of similar effluent into Zechstein formations (80–100 m deep), this resulted in an unknown degree of regional underground contamination which nowadays puts aquifers at risk and impairs drinking water catchment.

The presence of the "phenol lake" surface deposit provides a unique opportunity to study such wastewater and draw up remediation strategies. The first step is the remediation of the lake itself, which is regarded as a permanent source of groundwater contamination.

General characterisation of the deposit

When our work began in 1992, the lake had the following characteristics:

- Area 9 ha
- Water volume 2 million m^3
- Maximum depth 27 m
- Visibility depth 3 cm
- Oxygen content of the water 0
- Strong odour of organic sulphur compounds

In contrast to the original composition of the pyrolysis effluent, the water in the deposit had undergone sharp change (Ringpfeil et al. 1988).

2. Analytical characterisation of the deposit

2.1 Chemical analysis

The entire deposit can be divided into three different zones (Wießner et al. 1993):

Surface water

This zone is affected by the seasonal mixing of the water and extends to a depth of about 10 m.

Deep water

The deep water zone is characterised by a discontinuity layer with clear differences in concentration. It extends to a depth of 27 m in the middle of the lake. This zone accounts for about 50% of all the water in the deposit.

Sediment zone

The deep water merges into a sediment zone with a slimy, oily consistency. The solid bed of the lake is saturated with the components of the deposit.

Chemical analysis revealed no unexpected components, merely indicating high levels of phenolic compounds and ammonium – the main components of the original effluent. The

strong odour is attributable to various organic sulphur compounds which are difficult to analyse in detail owing to air sensitivity. Table 1 shows the distribution of the summarising parameters.

Table 1: Concentration profile of the two water zones characterised by selected summarising data (from 2 June 1992) (Wießner et al. 1993)

Depth (m)	Total phenols (mgL^{-1})	NH_4-N (mgL^{-1})	COD (mgL^{-1})	DOC (mgL^{-1})
Zone 1				
0	7	79	964	263
5	23	85	980	274
10	86	134	350	405
Zone 2				
15	202	221	2200	627
20	228	239	2290	689
24	219	250	2245	690

NH_4-N: Ammonium-nitrogen content, COD: Chemical oxygen demand. DOC: Dissolved organic carbon

The phenol levels in the sediment are summarised in Table 2:

Table 2: Concentration of phenols in the deposit sediment ($mg\ L^{-1}$)

Compound	Sample 1	Sample 2	Sample 3
Phenol	174	190	242
2-methylphenol	18	18	22
3- and 4-methylphenol	91	133	145
Total C2-phenol	116	115	95
Total C3-phenol	81	69	72
Total C4-phenol	82	49	81

As expected, polycyclic hydrocarbons occur in higher concentrations in the sediment on the bed than in the water owing to their low solubility (Tables 3 and 4). Phosphate was not detected in the water; nor are any heavy metals present, as during pyrolysis they were unable to enter the condensation water.

2.2 Biological analysis

The phenolic pollutants are known to be microbiologically degradable under aerobic conditions. However, under anaerobic conditions there are evidently some limitations to their biodegradation (Fedorak and Hrudey 1984, Suflita et al. 1988, Fox et al. 1988, Rudolphi et al. 1991, Flyvbjerg et al. 1993). Although no oxygen was detectable in the whole deposit, aerobic bacteria were shown to predominate among the pollutant degraders: in the upper layers about 40–60% of the degraders of phenolic compounds were found in heterotrophic microbial communities (Becker et al. 1997). Neither nitrate-reducers nor sulphate-reducing or methanogenic consortia that degrade benzoate were detectable. Benzoate was used as a test substrate, as it is known to be the final aromatic intermediate (as activated benzoyl-coenzyme A) in the anaerobic transformation of several classes of aromatic compounds. Nitrite-reducing benzoate degraders were found with MPNs ranging from 0.03 to 20 ml. Although aerobic bacteria with specific degradation abilities are not likely to use their abilities under in-situ conditions, they represent a degradation potential which might be useful for aerobic remediation strategies. Figure x shows the cell counts of the culturable aerobic bacteria (and fungi) and the FDA-

hydrolysing viable bacteria in relation to the total bacterial count (acridine orange staining).

Table 3: **Concentration of PAH in the surface water and in 24 depth**(mg L^{-1})

	Surface	**Depth 24 m**
Naphthalene	0.13	210
Acenaphthylene	0.02	–
Fluorine	0.05	6.1
Phenanthrene	0.18	23.1
Fluoranthene	0.07	3.3
Pyrene	0.06	1.8
Benz(a)anthracene	0.01	0.7
Chrysene	0.006	2.8
Benz(b)fluoranthene	0.01	–
Benz(k)fluoranthene	0.005	0.4
Benz(e)pyrene	0.11	–
Benz(a)pyrene	0.01	0.5
Acenaphthene	0.03	6.5
Dibenzanthrazene	–	0.1

Table 4: Concentration of PAHs in the deposit sediment (mg kg^{-1})

Compound	**Sample 1**	**Sample 2**	**Sample 3**
Naphthalene	30	28	36
2-methylnaphthalene	31	30	33
1-methylnaphthalene	17	17	17
Total C2-naphthalene	119	91	102
Total C3-naphthalene	163	120	116
Total C4-naphthalene	130	101	131
Acenaphthylene	1.8	2.6	1.4
Acenaphthene	5.1	6.0	4.1
Fluorene	19	27	26
Phenanthrene	38	52	49
Anthracene	21	20	17
Fluoranthene	10.4	8.1	7.9
Pyrene	0.1	9.6	8.2
Benz(a)anthracene	1.1	0.7	0.7
Chrysene	3.0	1.6	1.8
Benz(k und b)fluoranthene	0.01	0.02	–
Benz(e)pyrene	0.2	?	?
Total methylphenanthrene and methylanthracene	40	24	25
Total C2-phenanthrene and C2-anthracene	24	16	19

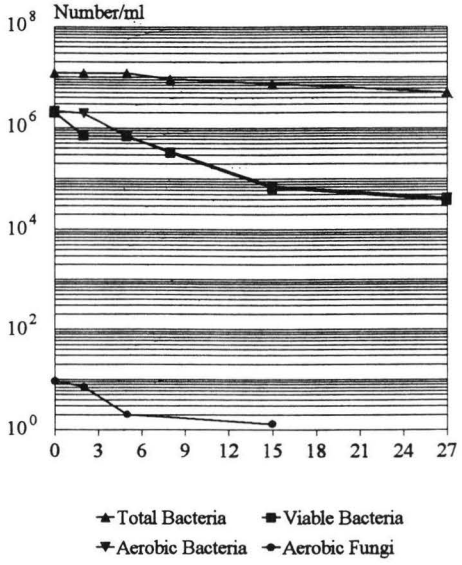

Figure 1: Cell counts of various ecophysiological groups (Becker et al. 1997).

2.3 Hydrogeological situation

Geological surveys are very important for assessing the potential risk. Moreover, the geological conditions must also be taken into account by the remediation strategy. The following local situation description was obtained with the help of deep drilling.

Hydrogeological studies indicate there are several quaternary and tertiary aquifers in the region of the lake. The main quaternary aquifer (known internally as GWL 18), which has a maximum thickness of 3 m, is comprised of a range of materials from sand to gravel and has a hydraulic conductivity of 10^{-4} m/s. It may be directly linked to the lake. The other quaternary aquifers (GWL 13-16) are only located regionally and have only a limited impact on the hydrogeology around the lake. The predominant quaternary geological material is a glacial deposit ('Geschiebemergel'), which is comprised of clay and silt material, and has a hydraulic conductivity of 10^{-6} to 10^{-9} m/s.

The most important tertiary aquifers are the upper (GWL 52) and lower (GWL 61), which are located beneath the main coal seam (seam 2.3) and the Luckenauer clay. They are probably not intercepted by the lake and are divided by another clay and silt layer of approximately 10 m thickness. Estimates of the hydraulic conductivity of the upper aquifer (10^{-4} to 10^{-3} m/s; with a thickness of 12–18 m) generally exceed those for the lower aquifer (10^{-5} to 10^{-4} m/s; with a thickness of 10 m). Both aquifers slope downwards from the south-west, where they are at depths of 10 m and 34 m, to the north-east, where the maximum depth of aquifer 52 is 70 m. Aquifer 61 is not reached by a well in this area. The former coal seam had a maximum thickness of 17 m and can be seen to have been divided into different layers by intermixed silt and sand lenses. It has been removed in the old coal mining area and replaced by spoil.

3. Behaviour of the deposit

AHS - anthropogenic humic substances

During laboratory analysis, the deposit water was found to contain a number of peculiarities requiring further explanation. The deposition of the pyrolysis water in the open air for a period of decades triggered a chemical process which led to the formation of macromolecules. This abiotic oxygen demand which in the freshly created effluent accounted for up to 8% of the entire oxygen demand (Ringpfeil et al. 1988), was caused by the known polymerisation of substituted phenols into compounds similar to humic substances. These were black in colour and in the case of the deposit being studied affected both the hydrodynamic behaviour and seasonally-dependent water circulation by reduced depth warming. We denoted this group of anthropogenic compounds "anthropogenic humic substances" (AHS), as they behave similarly to natural humic substances in terms of structure, sorption and reaction.

It was also shown that just as in the case of the extensive studies of the behaviour of pollutants in the presence of natural humic substances in soil, polar organic compounds are deposited into the humic substance matrix (Pörschmann and Stottmeister 1993). pH-dependent extraction reveals the reversible bonding of various polar aromatic compounds such as 2,4-dinitrophenol, 4-nitrophenol and 2-methyl-4.5.dintrophenol.

However, alkyl-substituted phenols relevant for the deposit such as 2- and 3-methylphenol and 2,4-dimethylphenol were not strongly bound by dissolved AHS – a result observed for both surface and deep water. This means that the reversibly sorbed contaminants are accessible to both for biotic and abiotic degradation processes.

Physicochemical and biological interactions

The sorption coefficients of various organic pollutants on AHS was predicted by correlating the K_{OC} and K_{OW} values of hydrophobic solutes in aqueous solution (Kopinke et al. 1995). The theoretically based concept enables the sorption coefficients (K_{OC} or K_{DOC}) of nonpolar solutes to be estimated based on their octanol-water-partition coefficients (K_{OW}) – and the solubility parameters of the polymer and sorbates. Furthermore, experimentally measured sorption coefficients permit calculation thereof, producing a figure of about 12.5+0.5 $(\text{cal cm}^{-3})^{½}$ for humic substances

The interactions between the low molecular weight contaminants of the deposit water and the humic-like polymeric substance are important for microbiological degradation processes. Martius et al. (1996) describe the degradation efficiency and molecular size alteration of dissolved organic matter during the aerobic microbial treatment of waters from the deposit. Biological degradation is evidently overlapped by abiotic oxidation and agglomeration. The dissolved organic content is characterised by stepwise micro- and ultrafiltration to estimate the ratio of humic-matter-like macromolecules and low molecular substances, as well as their changes during aerobic treatment. It was shown that microbiological DOC elimination was limited to 65% under optimised conditions (nutrient addition, adapted mixed cultures, aerated fermenter). Biodegradation mainly occurs in the fraction below 0.5 kDa (30%) and 0.5–1 kDa (12%). The degree of removal is negligible in the ranges 1–3 kDa (0.8%) and 3–5kD (2 %), whereas in the fraction >0.3 µm small but significant DOC reduction (6%) was observed, which was most probably due to bioadsorption.

4. The fate of contaminants

The aims of the studies described above were the remediation of the deposit and to obtain fundamental insights into the behaviour of the similar waters in the groundwater zones not only around the lake but in the whole contaminated region.

The black water is coloured by the AHS. One typical reaction of dissolved humic matter is flocculation with Al^{+++} or Fe^{+++} salts. Under defined conditions, flocculation of the deposit water was possible, forming a clear colourless water with decreased toxicity and organic load (cf. Table 6)

Table 6 Decrease of contaminants and decoloration of the deposit water by flocculation with ferric salts
(laboratory and in situ enclosure experiments)

Parameter	Decrease in %	
	Laboratory experiments	Enclosure experiments
Aromatic compounds[1)]	78	75
Colour[2)]	95	93
Turbidity[3)]	98	95
COD	55	47
TOC	60	55
Ammonium nitrogen	6	7
Water steam volatile phenols	0	0
Toxicity[4)] (surface water)	94	

1) Optical density at 270 nm
2) Optical density at 440 nm
3) Optical density at 650 nm
4) EC50-value with *Photobacterium phosphoreum* after 30 min

The promising results of the in situ enclosure experiments led to the need for larger enclosure systems to study:

- flocculation and neutralisation technology
- the sedimentation of the flocs
- oxygen input via the surface
- the abiotic reoxidation of dissolved phenolic compounds
- the activation of the indigenous microbial biocenoses
- the need for nutrients
- the development of aquatic biology

In order to carry out these studies, a large in situ enclosure (33 m diameter, 26 m deep, with a volume of some 20,000 m^3, and a surface area of around 855 m^2) was erected. This enclosure was filled with original water from different depths of the surrounding waste water deposit, such that the average pollutant concentration corresponded to a depth of about 10 m.

Flocculation was carried out with 46m^3 $FeCl_3$ solution (40wt%) at a pH of 4.5. Afterwards, the water was neutralised with 41 m^3 $Ca(OH)_2$ suspension (20 wt%) to achieve a pH of about 7.0.

The enclosure can be considered as a "pond within a lake", representing a model of the seasonally-dependent mixing of the water body and the oxygen input via the surface.

The course of the DOC (depicted in Fig. 2) characterises the various periods of treatment, flocculation, the acidic interim phase, and decrease caused by re-establishing microbiological activities.

On the basis of these pilot-scale experiments, the whole wastewater deposit was flocculated and neutralised. At the present time, the water body has a yellow tinge at the surface and is colourless with a visibility depth of a few meters. Chemical and biological changes are being studied and the results of this unique experiment will be reported in the near future.

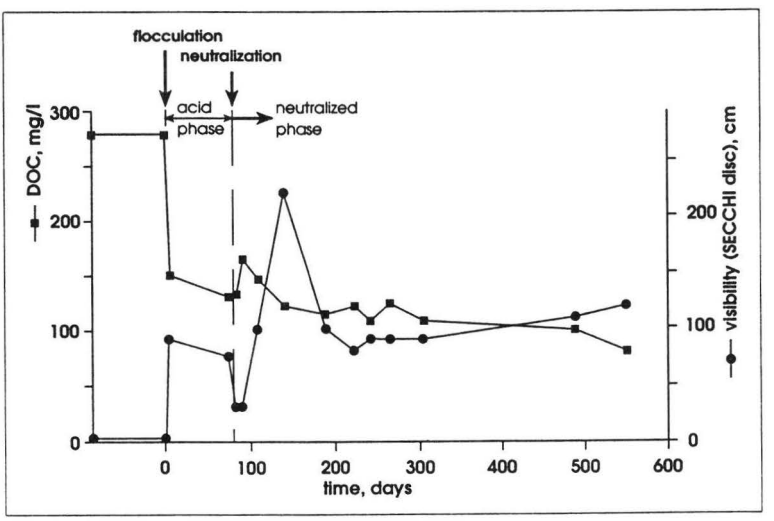

Figure 2: Decrease of DOC in *in situ* enclosure experiments (1 m depth) (Stottmeister et al. 1998)

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ASSESSMENT OF THE BIOAVAILABILITY OF SOIL POLLUTANTS USING LUX-BASED BIOSENSORS: AN INTER-DISCIPLINARY APPROACH

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Key words: bioavailability, biosensors, heavy metals, chemical speciation

SUMMARY

A suite of *lux*-based biosensors and Microtox™ were used to determine the bioavailability of a heavy metal pollutants present in interstitial pore water samples obtained from two long term sewage sludge field trials, one at Braunschweig, Germany and the other at Gleadthorpe, UK. Both the *lux*-based biosensors and Microtox™ were sensitive to high concentrations of these pollutants, especially with longer exposure times. The combined biological and chemical approaches highlighted the importance of the free metal ion concentrations in predicting the response of the biosensors to the pollutants. This study demonstrated the potential of using a suite of *lux*-based biosensors to detect the bioavailability of pollutants and therefore report on soil health.

KURZFASSUNG

Eine Reihe von *lux*-basierten Biosensoren und Microtox™ wurden benutzt um die Bioverfuegbarkeit von Schwermetall Schadstoffen zu bestimmen in Proben interstitiellen Porenwasser von zweier langzeit Klaerschlamm Feldversuche, einer bei Braunschweig, Deutschland und der anderer bei Gleadthorpe, UK. Beide, die *lux*-basierten Biosensoren und Microtox™, waren gegen hohe Konzentrationen dieser Schadstoffe empfindlich, besonders nach laengerer Expositionszeit. Die kombinierten biologischen und chemischen Ansaetze heben die Wichtigkeit der Konzentrationen der freien Metalionen fuer die Voraussage der Reaktion der Biosensoren auf die Schadstoffe hervor. Diese Studie demonstriert das Potential der Nutzung einer Reihe von *lux*-basierten Biosensoren zum Nachweis der Bioverfuegbarkeit von Schadstoffen und um folglich ueber die Bodenqualitaet zu berichten.

RÉSUMÉ

Un groupe de bioindicateurs *lux*-based et Microtox™ ont été utilisé pour déterminer la disponibilité biologique de métaux lourds pollutants présents dans des échantillons d'eau provenant de pores intersticiels qui ont été échantillonés dans deux stations expérimentales d'épandage à long terme de boues d'épuration, une situé à Braunschweig, en Allemagne et l'autre située à Gleadthorpe en Grande Bretagne. Autant les bioindicateurs *lux*-based que Microtox™ étaient sensibles à des concentrations élevées de ces pollutants, principalement après de longues expositions. Une approche biologique et chimique combinée a montré l'importance des concentrations d'ions metalliques libres pour prédire la réponse des bioindicateurs aux pollutants. Cette étude a demontré le potentiel de l'utilisation d'un groupe de bioindicateurs *lux*-based pour déterminer la disponibilité biologique de pollutants et donc rendre compte de l'état de santé du sol.

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INTRODUCTION

The European Urban Waste Treatment Directive (Council of European Communities, 1991) states that the practice of sewage sludge disposal at sea should cease. One of the most viable alternatives to sea disposal is the application of sewage sludge to agricultural land. The latter has further been encouraged since sewage sludge can be a beneficial source of nutrients and act as a soil conditioner (Smith, 1991). However, of particular concern is the fact that sewage sludge contains heavy metals at levels above those found in agricultural soils. The residence times of heavy metals in soils are of several thousand years (McGrath, 1994) and therefore continual application of sewage sludge to land will result in a build up of heavy metals. There is a lack of understanding of the field scale implications of long term sewage sludge additions. Decreases in the microbial biomass of soils due to the presence of heavy metals resulting from past applications of sewage sludge have been reported (Brookes and McGrath, 1984). Recently a recommendation to lower the U.K. soil limit for Zn (MAFF/DoE, 1993) has been adopted by the U.K. Government in the voluntary Code of Practice for Agricultural Use of Sewage Sludge. However, legislation is still based on total concentration of heavy metals in soil, although it is the free metal ion concentration in the soil solution which is toxic to biological organisms (McGrath, 1994). Therefore a more appropriate legislative approach is required.

The monitoring of heavy metal toxicity in soils requires the development and use of rapid and reliable ecotoxicity tests. Conventional analytical techniques, although accurate, are expensive, time consuming and require a wide range of laboratory facilities. The development of biosensors for environmental monitoring has recently gained much attention due to their rapidity, low cost and portability. Biosensors are analytical devices incorporating a biological sensing element (e.g. enzymes, microorganisms, antibodies etc) either linked with or integrated within a physicochemical transducer (e.g. acoustic, colorimetric, optical and electrochemical transducers) (Dennison and Turner, 1995). Biosensors have the added advantage over analytical techniques in being able to integrate a broad range of soil environmental factors (pH, Eh, exchangeable cations, organic matter, etc) that determine the bioavailability of pollutants (Holmes *et al.*, 1993)). Luminescence-based biosensors are increasingly used as sensitive technique in ecotoxicity testing (Steinberg *et al.*, 1995). The Microtox assay (Azur, Bucks), which uses the naturally luminescent marine bacterium *Vibrio fishceri*, has been shown to be sensitive to a number of pollutants in various environments making it an international benchmark in ecotoxicity testing. However, the Microtox™ assay requires the alteration of pH and the addition of a saline buffer, both of which alter the chemical speciation of the test media and the pollutants. Furthermore, the use of a marine organism for terrestrial ecotoxicity testing has been questioned. The ability to insert the genes responsible for luminescence (the *lux* gene cassette) into ecologically relevant test organisms may provide a more appropriate ecotoxicity test. Paton *et al* (1995a) has demonstrated the ability of *lux* modified constructs of *Pseudomonas fluorescens* to assess the bioavailability of heavy metals in aqueous solutions. Furthermore, l*ux*-based biosensors have been shown to respond to pollutants with a higher level of sensitivity than enzyme assays, ATP

luciferin-luciferase assays, respiration or growth inhibition studies (Paton *et al.*, 1995b; Brown *et al.*, 1996; Paton *et al.*, 1997).
The aim of this paper was to use *lux*-based biosensors and established chemical speciation techniques to assess the bioavailability of heavy metals in two sites which were highlighted in the MAFF/DoE (1993) report as being relevant for sewage sludge field analysis: Braunschweig, Germany and Gleadthorpe, UK. The use of these field sites is essential in predicting the long term fate and toxicity of anthropogenically derived pollutants in the soil environment.

MATERIALS AND METHODS

Soils

Field moist soils from Braunschweig, Germany were collected from plots on a site cleared from forest in 1950 which received either unamended or heavy metal amended sewage sludges from 1980 to 1990. Soils (field moist) from Gleadthorpe Experimental Husbandry Farm were collected and from plots polluted with Zn, Cu, Ni and Cd as a result of the addition of sludges enriched with increasing concentrations of Zn and/or Cu, singly or in combination in 1982 and again, in some cases, in 1986.

Extraction and chemical analysis of the soil solution

Soil solution was extracted from soils from the two sites using soil moisture samplers from Rhizosphere Research Products (Eijelkamp, Holland) according to the procedure described by Knight *et al.*, 1996. Soil solution pH was measured using a glass electrode. Dissolved organic carbon (DOC) was measured using an automated PPM LABTOC analyser. The concentrations of Zn, Cu, Ni and Pb were determined by Inductively-Coupled Plasma Atomic Emission Spectrometry (ICP-AES) while Cd was measured by Graphite Furnace Atomic Absorption Spectrometry (GF-AAS). Free Zn^{2+} was determined using a cation exchange resin method (Knight and McGrath, 1995).

Determination of pollutant bioavailability using Microtox™ and lux-based biosensors

Three microorganisms containing the *lux* cassette were used as biosensors: *Escherichia coli* HB101 pUCD607 (Rattray *et al.*, 1990), *Pseudomonas fluorescens* 10586s/r pUCD607 (Amin-Hanjani, 1993), *Rhizobium leguminosarum* biovar *trifolii* TA1 *lux*AB (Paton *et al.*, 1995b). The *lux*-based biosensors were stored as freeze-dried cultures and resuscitated according to standard laboratory protocols (Paton *et al.*, 1997). All acute assays with the biosensors, including Microtox™, consisted of adding 50 or 100 µl of the appropriate cell suspension, previously resuscitated from a freeze dried vial, to 450 or 900 µl of the test solution respectively, in a cuvette at 15 second intervals. The luminescence of the cells was then measured in a Bio-Orbit 1253 luminometer, after exposure times (E_t) ranging from 15 to 145 minutes. The assays were carried out in triplicate and the results expressed as a percentage of the luminescence measured in soil solutions from control plots which were amended with uncontaminated sewage sludge.

Table 1. Soil solution dissolved organic carbon, pH and heavy metal concentrations in both soil and soil solution.

Sewage sludge field trials	DOC ($mg\ l^{-1}$)	soil solution pH	HM in soil ($mg\ kg^{-1}$)		HM in soil solution ($\mu g\ l^{-1}$)		Zn^{2+} in soil solution ($\mu g\ l^{-1}$)
			Zn	Cu	Zn	Cu	
Braunschweig, Germany							
No sludge	20.6	5.1	43	9.8	168	11	105
Unamended sludge (100 $m^3\ ha^{-1}\ yr^{-1}$)	26.6	5.0	87.8	16.5	987	33	835
HM amended sludge (100 $m^3\ ha^{-1}\ yr^{-1}$)	23.4	5.0	162.5	37.1	2086	55	2043
Unamended sludge (300 $m^3\ ha^{-1}\ yr^{-1}$)	37.4	4.6	184.7	32.3	7437	108	6524
HM amended sludge (300 $m^3\ ha^{-1}\ yr^{-1}$)	38.6	4.4	294.6	91.6	25114	368	22007
Gleadthorpe, UK							
No Sludge	21.9	6.5	44	9	55	13	53
Uncontaminated sludge	14.6	6.3	53	11	205	25	29
Zn-sludge (633 $kg\ ha^{-1}$)	24.7	6.0	141	16	1384	25	657
Zn-sludge (1191 $kg\ ha^{-1}$)*	28.4	5.7	278	15	5465	30	2627
Zn-sludge (1896 $kg\ ha^{-1}$)*	29.3	5.6	291	21	10907	45	5087
Zn-sludge (2763 $kg\ ha^{-1}$)*	28.6	5.4	441	22	19711	45	9199
Zn:Cu-sludge (295:258 $kg\ ha^{-1}$)*	31.2	6.2	94	58	675	120	380
Zn:Cu-sludge (916:124 $kg\ ha^{-1}$)*	28.4	5.3	189	86	5765	175	2398
Zn:Cu-sludge (1557:101 $kg\ ha^{-1}$)*	29.9	5.3	230	159	10850	360	4755
Zn:Cu-sludge (2299:16 $kg\ ha^{-1}$)*	36.6	5.4	328	223	18685	600	6277
Cu-sludge (1121 $kg\ ha^{-1}$)*	25.7	6.0	75	150	400	250	208
Cu-sludge (1278 $kg\ ha^{-1}$)	22.9	6.2	57	160	255	240	108
Cu-sludge (2077 $kg\ ha^{-1}$)*	25.8	6.0	69	254	425	340	184
Cu-sludge (2968 $kg\ ha^{-1}$)*	28.0	5.5	73	349	1015	620	399

*Sludge was applied in 1982 and 1986; data presented are the means; DOC = Dissolved Organic Carbon; HM = Heavy Metal.
Data for the concentrations of Cd, Ni and Pb in soil are not presented as they were below UK limits (UK SI 1263, 1989).

Statistical analyses

Microsoft Excel (version 5) and Genstat 5 for Windows (release 3) were used to carry out all statistical analyses which included multivariate analysis, principle component analysis and linear regression.

RESULTS AND DISCUSSION

Both sewage sludge field trials consisted of plots exhibiting a wide range of Zn concentrations, from levels less than 20 % to 150 % of the current UK permitted Zn loading limits (Table 1). The concentrations of copper were lower in Braunshweig than in Gleadthorpe, the latter containing 4 times the level of copper than the former in some plots. The DOC levels at both sites were also similar, ranging from 15 mg l^{-1} to 39 mg l^{-1} (Table 1). One of the most striking differences between the two sites is their solution pH, the pH of the soil solutions from Braunshweig ranging from 4.4 to 5.1, and from 5.3 to 6.5 for Gleadthorpe. The more acidic conditions at the Braunschweig sites resulted in greater amounts of Zn in the soil solution compared to Gleadthorpe (Table 1). The increased Zn in soil solution also resulted in comparable increases in the free Zn^{2+} concentration in the soil solution (Table 1).

The luminescence of *P. fluorescens* 10586s pUCD607 was reduced to 50 % at sites receiving 175 mg Zn kg^{-1} soil (data not shown) although the total Zn in the soil solution accounted for only 32 % of the variance in the data set (Table 2). A more accurate predictor of the luminescence response to the toxicity of Zn was provided by the free Zn^{2+} concentrations in soil solution, the latter explaining 65 % of the variance in the data (Table 2).

Table 2. R^2 values obtained in the regression analyses of the response of the luminescence-based biosensors to pollutants in the soil solution.

Biosensor	Exposure time (min)	HM in soil solution (μg l^{-1}) Zn	Cu	Zn^{2+} in soil solution (μg l^{-1})
Braunschweig, Germany				
P. fluorescens	45	32	nd	65
Gleadthorpe, UK				
Microtox™	15	85	17	nd
R. leguminosarum	37	75	3	86
P. fluorescens	15	89	13	84
P. fluorescens	35	30	58	nd
P. fluorescens	60	40	49	nd
E. coli	25	78	2	nd
E. coli	77	93	1	nd
E. coli	145	95	3	96

nd = not determined

The response of the various luminescence-based bioassays to the soil solutions obtained from plots at the Gleadthorpe experiment which received Zn-contaminated sewage

sludge is shown in Figure 1. Microtox™ and *E. coli* were the most sensitive to the heavy metals present (Fig. 1).

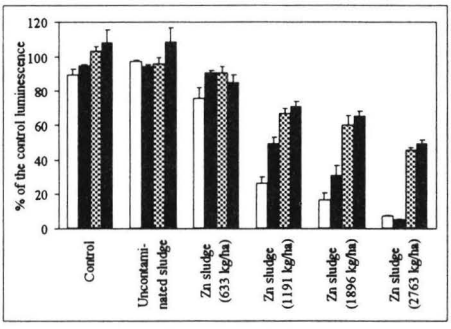


Fig. 1

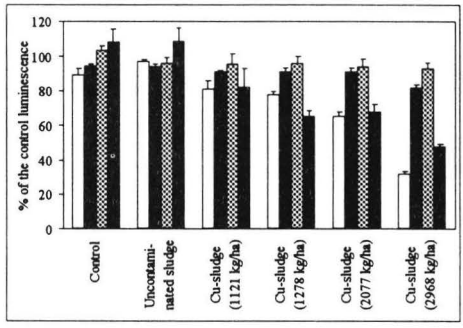
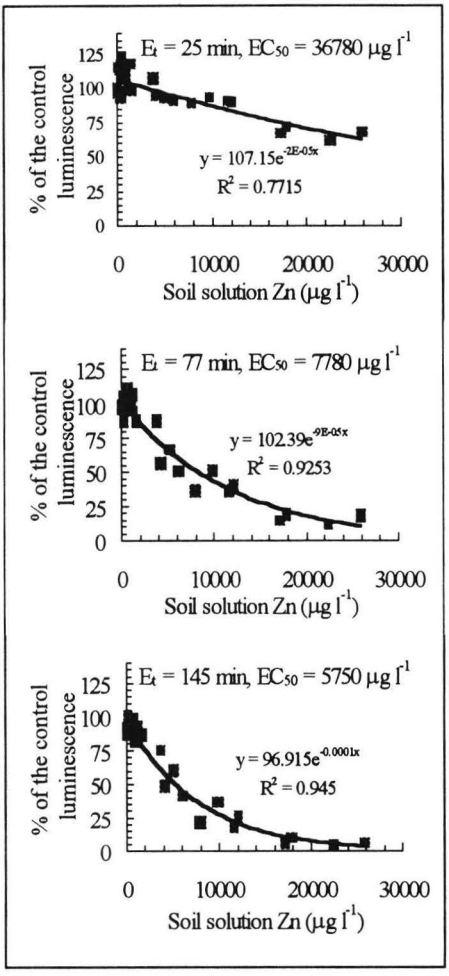


Fig. 2

Legend for Figures 1, 2 and 3
Each individual bar represent a different *lux*-based ecotoxicity biosensor; these are from left to right: *E. coli*, Microtox, *R. trifolii*, *P. fluorescens*

Figure 2, which shows the response of the suite of assays to Cu shows a significantly different order of sensitivities for biosensors when compared with Figure 1. *P. fluorescens* is more sensitive to Cu than Microtox or *R. trifolii*. *E. coli* still seems to express a high level of sensitivity. This observation has been made in aqueous solutions also (Paton *et al.*,1995a). When both Cu and Zn are present in the soil solution (Fig 3) the pattern becomes further complex with no expression of luminescence by Microtox at the two highest concentrations at which *E. coli* is also found to be greatly inhibited.
Each of these organisms represent different ecological niches. All of them are Gram-negative. *P.fluorescens* is a vigorous colonising rhizobacterium which is ubiquitous in terrestrial systems. *R. trifolii* is a root symbiont that plays a particularly important role in temperate arable and grassland systems. An important characteristic of this organism is the associated high levels of polysaccharides that are exuded and may create a protective mechanism against pollutants while the organism is in a free-living stage in the soil. *E. coli* is a sensitive laboratory isolate while Microtox uses the marine organism *V. fischeri*. The three graphs (Figs. 1, 2 and 3) suggest that the non-indigenous soil organisms are particularly sensitive to the metal loads studied but this means that when translating their responses to terrestrial matrices caution must be exercised.
It is unlikely that in arable systems, single metal pollutants will exist and therefore particular emphasis should be placed on interpreting the results associated with Figure 3. It has been predicted that the effects of combined metal pollutants caused an inhibition of luminescence expression greater than that explained solely by additive effects. This is a very significant finding as legislative limits are currently based on the total concentration of individual metals with no regard for potential anatagonistic or synergistic interaction that may be associated with these target pollutants.
In addition to considering the impact of a concentration gradient on the response of the biosensors it is also important to consider a temporal aspect too. Figure 4 represents the



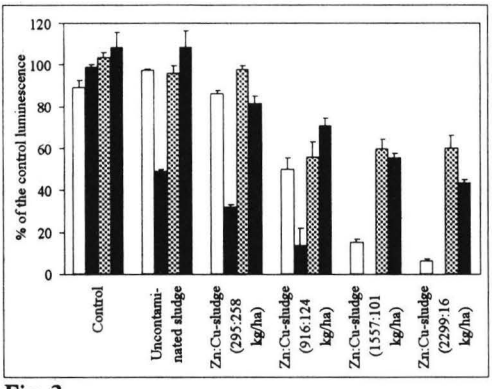


Fig. 3.

deleterious effect of Zn on the response of *E. coli* at 25, 77 and 145 minutes in soil solution from the Gleadthorpe site. A distinctive change in the gradient of the dose response curve can be clearly identified, as can a corresponding drop in the EC_{50} value. Enumeration of colony forming units ensured that this was an acute assay. The response characterised here in Figure 4, was observed for all of the selected biosensors used for the Gleadthorpe experiment. This temporal response highlights the need to express dose response results in conjunction with time to ensure the robustness of these biosensors between laboratories.

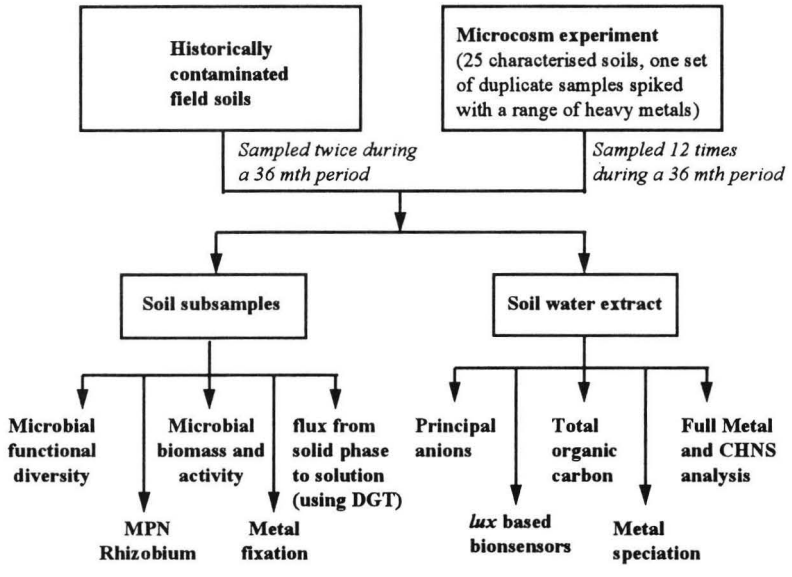
Fig. 4.
Temporal effect of Zn on *E. coli*

CONCLUSIONS

It is inevitable that there will be a dramatic increase in the land area which will be used for the application of sewage sludge. This in turn means that the level of heavy metals and organoxenobiotics in these soils will rise with time. To predict the long term impact of these pollutants, their partitioning in soil systems and their bioavailability we must couple new technologies with traditional biological and chemical approaches. In particular we must value the resource of long term field trial where the impact of ageing can be scrutinised. The application of *lux*-based biosensors to soil interstitial pore water represents a sensitive technique to study the impact of pollutants in soil systems.

CURRENT RESEARCH COLLABORATIVE PROGRAMME

Many questions connected with the impact of ageing on soils remain unanswered. To begin to probe these issues, the Biotechnology and Biological Sciences Research Council (Chemical and Pharmaceutical Directorate) are resourcing a multicollaborative project which is focusing on the temporal change of metal toxicity in soils.



There are two principal parts to the experiment. The first part involved assessing heavy metal bioavailability in historically contaminated sites such as Woburn, Braunschweig and Gleadthorpe, which were highlighted in the MAFF/DoE (1993) report as being relevant for sewage sludge field analysis. The second part involved setting up a large microcosm experiment to assess the effect of soil ageing on heavy metal bioavailability in the soil environment. A range of novel chemical and biological techniques (Fig. 1) are used to assess heavy metal availability in subsamples of the bulk soil and pore water. Fluxes of labile species within soils are measured using the *in situ* procedure of diffusion gradients in thin films (Davison and Zhang, 1984), metal ion fixation is measured using isotope dilution techniques (Nakhone and Young, 1993), and chemical speciation is measured using ion exchange equilibria (Holm *et al.*, 1995). Microbial parameters are measured using conventional techniques and *lux*-based biosensors (Paton *et al.*, 1997).

This holistic approach is significantly enhancing our understanding of the relationship between concentration and temporal fluxes and the resupply of metals to the labile phase. By integrating our chemical interpretation with biological indicators it is anticipated that this work will be of great importance to legislatures and regulators.

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BIOREMEDIATION POTENTIAL AS INFLUENCED BY THE PHYSICAL STATES OF PAH POLLUTANTS

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Key words: bioavailability, biodegradation, mass transfer, PAH, physical states

SUMMARY

Mass transfer models and biodegradation models were developed for three theoretical physical states of PAHs in soil. These mechanistic models were used to calculate the treatment periods necessary for complete removal of the PAH pollutants from the soil under batch conditions. Results indicate that the bioremediation of PAHs in such systems is mainly mass transfer limited. The potential for bioremediation as a treatment technique for PAH contaminated soils is therefore mainly determined by the mass transfer dynamics of PAHs.

Contaminated Soil '98, Thomas Telford, London, 1998, 133–142

1. INTRODUCTION

The physical states in which polycyclic aromatic hydrocarbons (PAHs) are present in soil mainly determine the potential of remediation techniques. It must be analysed whether the mobility requirements of possible remediation techniques can be met in and by the physical status of the contaminant in the soil matrix (Rulkens and Bruning, 1995).

Bioremediation is a clean-up technology that was initially presumed to have great potential, but it became evident that just like the physical and chemical treatment techniques for polluted soil, biological methods had their disadvantages. Long treatment periods and high residual concentrations were the main problems. This is especially true for PAH-polluted soil. Because of their hydrophobicity and low water solubilities, PAHs strongly interact with the soil matrix and can even form separate phases. Micro-organisms can only degrade dissolved PAHs and so they have to be released from the solid phase to an aqueous phase in which they are available. As a result of low mass transfer rates in the soil matrix, this release is often limiting the effectiveness of bioremediation and we speak of a reduced bioavailability of the pollutants causing the reduced effectiveness.

On a theoretical basis, several simplified states of PAHs in soil have been suggested and mass transfer models are formulated to describe the release of PAHs from these different states to obtain an estimated time in which the PAHs concentration can be reduced by leaching processes (Rulkens and Bruning, 1995). The same procedure can be applied to bioremediation processes when microbial kinetics are incorporated into these models. Mathematical simulations of the combined mass transfer and microbiological conversion indicate the time needed to reduce the concentrations of the different PAHs to certain levels. Hereby the potential of bioremediation can be estimated and decisions can be made whether or not bioremediation should be attempted.

The aim of this paper is to translate the theoretical considerations concerning the mass transfer of hydrophobic pollutants in different physical states in the soil to the situation where micro-organisms can degrade the contaminants. The effect of several model parameters on the availability of pollutants towards microbial populations is illustrated with the results of mathematical simulations with model PAHs.

2. PHYSICO-CHEMICAL PROPERTIES OF PAHS

Polycyclic aromatic hydrocarbons are extremely hydrophobic compounds due to the absence of polar groups on the molecules. This results in very low water-solubilities and high octanol-water partitioning coefficients (Tab 1). Besides the solubility (C*) and the octanol-water partitioning coefficient (K_{ow}), there is little difference in the values of the other physico-chemical properties of the PAH listed in Table 1. Because diffusion coefficients depend mainly on the molar volume of the diffusing solute (Bird et al., 1960), the decrease of the diffusion coefficient with an increased number of aromatic rings is relatively small. Due to their hydrophobic nature, PAH have high solubilities in organic hydrophobic solvents. Because emissions of PAHs are often accompanied by spills of non-aqueous-phase-liquids, this is of importance for the physical state in which PAHs are present in the soil (Ghoshal and Luthy, 1998).

Table 1 *Physico-chemical properties (at 30°C) of some PAHs*

	M_w [a]	density [b]	diffusion coefficient [c]	C* [a]	log K_{ow} [a]
	[g mol]	[$10^3 \times$ kg m^{-3}]	[$10^{-10} \times$ $m^2 s^{-1}$]	[kg m^{-3}]	[-]
naphthalene	128	1.03	9.31	0.0317	3.37
acenaphtylene	152	0.899	8.35	0.00393	4.07
fluorene	166	1.20	7.88	0.00198	4.18
phenanthrene	178	0.980	7.70	0.00129	4.46
anthracene	178	1.28	7.70	0.000073	4.45
pyrene	202	1.27	7.05	0.000135	5.32
fluoranthene	202	1.25	6.90	0.00026	5.33
chrysene	228	1.27	6.44	0.000002	5.61

[a] Sims and Overcash,1983; [b] Weast, 1974; [c] calculated values (Bird et al., 1960)

3. PHYSICAL STATES OF POLLUTANTS

In an earlier study on the effect of physical states of soil pollutants on the remediation potential of physical separation processes (Rulkens and Bruning, 1995), 6 simplified physical states for soil contaminants were proposed on a theoretical basis. In this work, 3 of these states (Fig 1) are further analysed as far as the influence on the bioavailability and bioremediation potential is concerned.

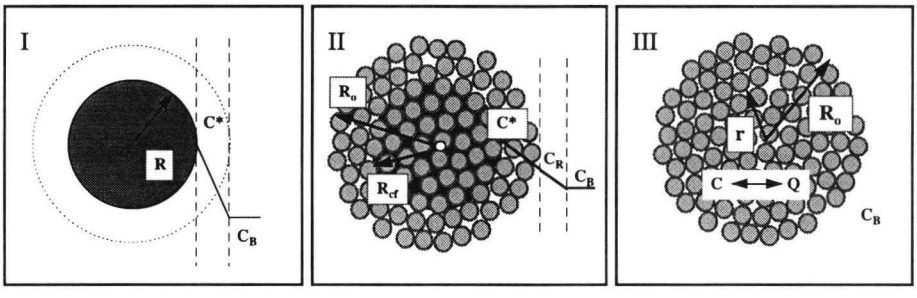


Figure 1 *Schematic presentation of three proposed physical states of PAHs in soil particles. Solid phase PAH as: pure particle (I), pure solid in a pore (II) and sorbed into a soil aggregate (III).*

For simplicity sake, only pure PAH contaminants are considered. The presence of non-aqueous-phase-liquids, which were mentioned before is neglected. However, with the methodology followed in this study, such systems can also be described by incorporating for instance the partitioning of PAHs into an organic phase.

The considered physical states are: pure PAH particles, PAHs which have formed pure solid phases in the pores of porous soil aggregates and PAHs that are intrapartically sorbed to soil organic matter. The first two states are likely to be found in heavily

contaminated situations (hot-spots), whereas the latter state is probable when diffusive emissions occurred.

4. MATHEMATICAL MODELS

In this section, three mass transfer models are presented to describe the fluxes of the contaminant to the bulk aqueous phase in which biodegradation is possible. These models are based on a mathematical description of microbial degradation kinetics and of mechanistic processes, using data on the physico-chemical properties of the contaminant and the porous soil matrix (e.g. situations II and III, Fig 1). The models describe the flux of contaminant from the spherical polluted particles to the bulk liquid and the loss of pollutant from these particlesand the biodegradation. The decrease in degree of contamination can therefore be calculated as a function of time.

4.1 Microbial growth and degradation kinetics

The growth of biomass on the contaminant dissolved in the bulk liquid phase can be described according to Monod kinetics. The growth rate (μ) is than expressed as a function of the maximal growth rate (μ_{max}), the affinity constant (K_s) and the dissolved PAH concentration (C_B) in the bulk liquid phase:

$$\mu = \mu_{max} \frac{C_B}{C_B + K_s} \qquad (1)$$

The development of the specific organisms growing on the dissolved PAH in time can be described by:

$$\frac{dX}{dt} = \mu X \qquad t=0,\ X=X_i \qquad (2)$$

where t is time, X the biomass concentration in the bulk liquid and X_i the initial biomass concentration. When the dissolved PAH concentration is high compared to the affinity constant, the biomass concentration increases exponentially in time due to zero order kinetics. When the PAH concentration is low compared to K_s (equation (1)), first order kinetics are observed. The degradation of dissolved PAHs is coupled to biomass growth by the yield coefficient ($Y_{x/s}$):

$$\frac{dC_B}{dt} = -\frac{1}{Y_{x/s}} \frac{dX}{dt} = -\frac{\mu X}{Y_{x/s}} \qquad (3)$$

When there is a supply of dissolved PAHs to the bulk liquid by dissolution or desorption, an additional term describing this mass transfer must be incorporated in equation (3). In this model for biodegradation of contaminants by specific populations, the growth of the micro-organisms on other carbon sources is neglected for simplicity sake.

4.2 Dissolution of pure PAH particles and subsequent biodegradation

The dissolution of pure PAHs particles in a well-mixed bulk liquid phase can be described by simple mass transfer equations (Rulkens and Bruning, 1995). The flux of a PAH to the bulk liquid phase is described by:

$$N = k(C^* - C_B) \qquad (4)$$

where N is the flux of the dissolved PAH over a stagnant fluid layer at the solid-liquid interface, k is the mass transfer coefficient and C* is the solubility of the PAH. The mass transfer coefficient k depends on hydrodynamic conditions and for small particles or

large particles at low relative velocities, the value of this parameter can be approximated by (Rulkens and Bruning, 1995):

$$k = \frac{D}{R} \qquad (5)$$

where D is the diffusion coefficient of the PAH and R is the radius of the PAH particle. The decrease in the particle radius in time can be expressed by:

$$\frac{dR}{dt} = -\frac{D}{\rho R}(C^* - C_B) \qquad t=0,\ R=R_{t=0} \qquad (6)$$

where ρ is the density of the PAH particle. A mass balance for one dissolving PAH particle with subsequent biodegradation in a space element with a volume of V is used to describe the evolution of the dissolved bulk PAH concentration in time:

$$\frac{dC_B}{dt} = \frac{4\pi RD}{V}(C^* - C_B) - \frac{\mu X}{Y_{x/s}} \qquad t=0,\ C_B=0 \qquad (7)$$

4.3 Dissolution of PAH from filled pores and subsequent biodegradation

In the case of pure solid-phase contaminant located in the pores of a soil particle (Fig 1, II), the dissolution of PAHs from these pores to the bulk liquid phase can be described with the 'shrinking-core model'. In this model, the contaminant front located at R_{cf} moves inwards as a result of the compound flux to the bulk. Assuming pseudo steady-state conditions, the total mass flux of pollutant (N_T) through the pores between R_{cf} and R_o to the solid-liquid interface can be described by:

$$N_T = -(4\pi r^2 \varepsilon) D_{eff} \frac{dC}{dr} \qquad R_{cf} \leq r \leq R_o \qquad (8)$$

where r is the coordinate in the direction of transport, ε the particle porosity, D_{eff} the effective diffusion coefficient through the water filled section of the pore (accounting for influences of pore tortuosity and constrictivity on liquid diffusion), R_o the radius of the particle and C the dissolved PAH concentration in the pores. Equation (8) can be integrated between R_{cf} and R_o assuming that N_T is constant due to the pseudo-steady-state conditions. The total mass flux from the particle solid-liquid interface to the bulk liquid can also be described by:

$$N_T = 4\pi\varepsilon R_o^2 k\left(C_{R_o} - C_B\right) \qquad (9)$$

where k is defined in equation (5) and C_{Ro} is the dissolved PAH concentration at the surface of the particle. Elimination of C_{Ro}, by using the integrated equation (8) and equation (9), yields the following expression for the total mass flux to the bulk liquid:

$$N_T = \frac{4\pi R_o^2 \varepsilon\, D_{eff} k}{D_{eff} + \left(\frac{1}{R_{cf}} - \frac{1}{R_o}\right) R_o^2 k}(C^* - C_B) \qquad (10)$$

The change of the location of the contaminant front as a function of time can be formulated by:

$$\frac{dR_{cf}}{dt} = -\frac{R_o^2\, D_{eff} k}{\rho R_{cf}^2 \left[D_{eff} + \left(\frac{1}{R_{cf}} - \frac{1}{R_o}\right) R_o^2 k\right]}(C^* - C_B) \qquad t=0,\ R_{cf}=R_o \qquad (11)$$

The concentration in the bulk liquid phase is described by an equation that follows from a mass balance:

$$\frac{dC_B}{dt} = \frac{4\pi\varepsilon R_o^2 D_{eff} k}{V\left[D_{eff} + \left(\frac{1}{R_{cf}} - \frac{1}{R_o}\right)R_o^2 k\right]}\left(C^* - C_B\right) - \frac{\mu X}{Y_{x/s}} \qquad t=0,\ C_B=0 \qquad (12)$$

4.4 Desorption from porous particles and subsequent biodegradation

Concentration profiles in porous particles, of radius R_o, with intrapartically sorbed PAHs can be described with the following partial differential equation (Mulder et al., 1997; Rulkens and Bruning, 1995):

$$\frac{\partial C}{\partial t} = \frac{D_{eff}}{1 + \frac{(1-\varepsilon)}{\varepsilon}\rho_P K_p}\left[\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right] \qquad 0 \le r \le R_o \qquad r=0,\ \frac{\partial C}{\partial r} = 0 \qquad (13)$$

where ρ_P is the solid matrix density. The sorption coefficient K_p describes the linear partitioning of the pollutant over the solid and liquid phase:

$$Q = K_p C \qquad (14)$$

where Q is the concentration of the sorbed pollutant on the solid phase. The flux of the dissolved PAH at the surface of the porous particle to the liquid phase (N_s) can be described by an expression that follows from the boundary condition at the surface of the particle:

$$N_s = -\varepsilon D_{eff}\left.\frac{\partial C}{\partial r}\right|_{r=R_o} \qquad (15)$$

Analogous to the two earlier models, the evolution of the dissolved bulk PAH concentration can be described by a mass balance incorporating the flux of the pollutant to the bulk liquid (of volume V per particle) and the degradation by micro-organisms:

$$\frac{dC_B}{dt} = \frac{4\pi R_o^2 N_s}{V} - \frac{\mu X}{Y_{x/s}} \qquad t=0,\ C_B=0 \qquad (16)$$

It is assumed that external mass transfer limitations outside the porous particles are negligible (Rulkens and Bruning, 1995).

4.5 Numerical approximation

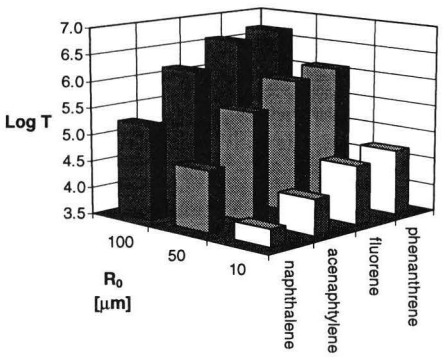
The models described in sections 4.1-4.4 cannot be solved analytically due to the non-linearity of the coupled (partial) differential equations. However, these equations can be numerically integrated to calculate the development of the variables (R, R_{cf}, C_B, X) in time. For the first two models, a fourth-order Runge-Kutta routine was programmed in FORTRAN to calculate the values of the model variables as a function of time (Press et al., 1992). The third model was solved numerically with the appropriate boundary conditions, using a Crank-Nicholson scheme (Press et al., 1992) programmed in a FORTRAN routine.

5. RESULTS AND DISCUSSION

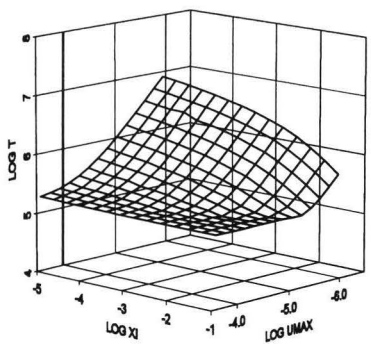
5.1 Biodegradation of pure PAH particles

When PAH pollutants have formed separate pure particles in the soil, the radius of the PAH particle and the solubility of the PAHs determine the time needed for complete dissolution of the particle (Rulkens and Bruning, 1995). It was expected that these factors also determine the potential of bioremediation and several mathematical simulations were performed to study this effect (Fig 2).

During these simulations, PAH concentrations of 1000 mg kg^{-1} dry weight of soil and slurry concentration s of 1:10 (m^3 soil)(m^3 aqueous phase)$^{-1}$ were assumed. The microbiological parameters were optimised so mass transfer limited biodegradation was assured. Results show (Fig 2) that, indeed, the particle radius of the PAHs is of great effect on the period that is required for biodegradation of the contaminant. Because the microbiological kinetics were optimised, dissolved aqueous phase concentrations were very low during degradation of the particles. Therefore, the times calculated for complete degradation of the pollutants by bacteria are the same to the dissolution times calculated in earlier work (Rulkens and Bruning, 1995).



Figuur 2 Influence of initial particle radius (R_0) and compound properties on the period needed for complete biodegradation.



Figuur 3 Effect of maximal growth rate ($UMAX \equiv \mu_{max}$) and initial biomass concentration ($XI \equiv X(t=0)$) on the period needed ($T \equiv t$) for complete biodegradation of a 100 µm naphthalene particle.

However, to assure mass transfer limited growth conditions, certain microbiological condition must be met. This is illustrated with Fig 3 were the effect of the maximal growth rate and the initial biomass concentration was determined in calculations on the biodegradation of a naphthalene particle. The plateau in the log T value (Fig 3) shows that an increase of microbiological capacity (maximal growth rate, initial biomass concentration), does not necessarily results in a shorter treatment period. In fact, this plateau indicates that the removal of PAH was mainly mass transfer limited instead of microbiologically limited.

During the simulation of the degradation of the high-molecular weight PAHs, low values were required for the microbiological parameters (yield, μ_{max}, K_s). Since these calculations have been made on model systems with one-component and one set of microbiological parameters, it might be an interesting exercise to study the effect of co-metabolism and multi-component PAH mixtures on system stability.

5.2 Biodegradation of PAH dissolving from filled pores

Simulations, similar to those described in section 5.1, were performed with the shrinking-core model (SCM). This model includes external mass transfer limitations in

contrast to earlier work (Rulkens and Bruning, 1995). It was calculated (Fig 4) that the incorporation of this extra mass transfer resistance at the outside of the particle results in a three-fold increase in the treatment period under complete mass transfer limited biodegradation conditions.

Comparison of Figs 2 and 4 indicates that the treatment period for both physical states are similarly affected by particle radius and compound properties. This agrees with calculations performed on the mass transfer dynamics in these two different systems (Rulkens and Bruning, 1995).

Experimental work on the influence of mass transfer on the biodegradation and bioavailability of PAHs has been done for the systems described in section 4.2 and 4.4 (Mulder et al., 1997; Mulder et al., 1998; Volkering, 1996). In these studies, the effect of the physical states of PAHs on the development of dissolved PAH and biomass concentrations were measured and modelled. However, such experiments have not been done on the system in which pores of porous particles are filled with solid-phase PAH. Therefore, we have now calculated the evolution in time of the contaminant front, the biomass and dissolved PAH concentration for the batch degradation of solid-phase naphthalene located in the pores (ε=0.05) of a 50 μm or a 100 μm soil particle (Fig 5).

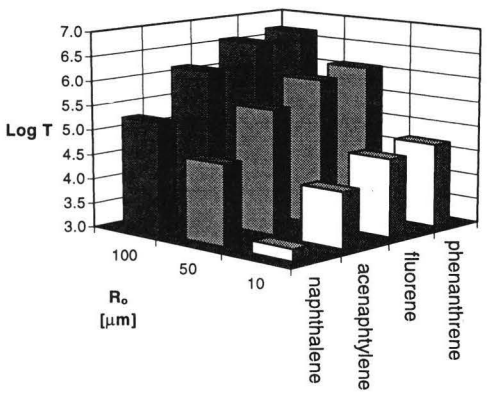


Figure 4 *Influence of particle radius (R) and compound properties on the period needed for complete biodegradation (ε=0.05).*

The results in Fig 5 are very similar to experimental findings with respect to the biodegradation of pure solid-phase PAHs (Mulder et al., 1998; Volkering, 1996). In such batch experiments an initial microbiologically limited degradation phase was observed with relatively high dissolved PAH concentrations. Thereafter, the biodegradation capacity exceeds the mass transfer rate due to the increased biomass concentration. At the transition point between

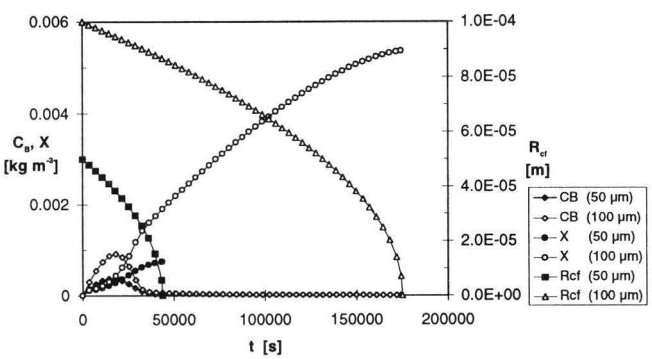
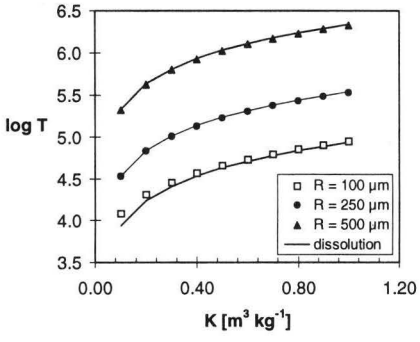


Figure 5 *Effect of particle radius (50 or 100 μm) on the batch biodegradation of naphthalene, dissolving from the pores of a soil particle: development of bulk biomass (X) and dissolved naphthalene (C_B) concentrations and the contaminant front (R_{cf}) in time.*

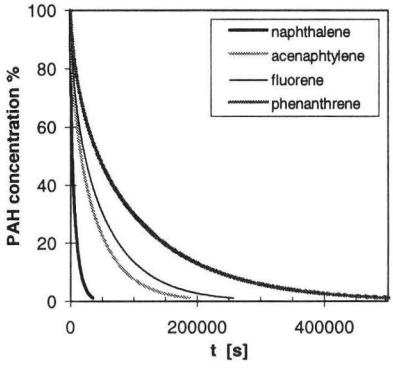
reaction and mass transfer limited biodegradation, the dissolved PAH concentration becomes very low and the driving force for mass transfer from the particle to the bulk liquid is maximised. Although the dissolved PAH concentration is very low during the mass transfer limited degradation phase, the biomass concentration still increases due to the partial conversion of contaminant to biomass. The maximisation of the driving force for mass transfer by reducing the dissolved PAH concentration to a very low value results in great similarity between treatment periods calculated on the basis of mass transfer models solely (Rulkens and Bruning, 1995).

5.3 Biodegradation of PAH desorbed from porous particles

When PAHs are sorbed into porous particles, the description of the flux of the desorbed contaminant to the bulk liquid becomes somewhat more complicated compared to the other two systems (section 5.1-2). To investigate whether the simple mass transfer models in a earlier study (Rulkens and Bruning, 1995) are also valid to indicate the period needed for complete bioremediation of such contaminated soils, simulations were performed with the model presented in section 4.4 (Fig 6).



Figuur 6 *Period (log T) needed for 99% naphthalene removal from porous particles of different radii (R) and sorption coefficients (K). Drawn lines are calculations (Rulkens and Bruning, 1995) and represent the shortest periods needed for 99% removal by leaching processes.*



Figuur 7 *Model calculations predicting the batch biodegradation of four PAHs sorbed to porous soil particles (R=200µm). Sorption coefficients were correlated to the K_{ow} value by: logK~log K_{ow}.*

Results (Fig 6) show that simple mass transfer models (Rulkens and Bruning, 1995) can adequately predict the period of time needed to lower the total PAH concentration in the particle to a level of 1 % of the initial amount. However, mass transfer limited degradation conditions must be assured. The slight deviation of the log T values for the 100 µm particle at low values of K from the dissolution model was caused by the relatively low initial biomass concentration assumed. Because the biodegradation was not directly mass transfer limited at the beginning of the simulation, the value of log T increased (see also Fig 2).

Under mass transfer limited biodegradation conditions, an increase of PAH sorption (K) or the particle radius (R) significantly increases the period needed for complete removal

of the PAHs. Because the sorption to hydrophobic material increases significantly with increasing PAH molecular weight (Tab 1), relatively longer bioremediation periods are needed for removal of the high-molecular weight PAHs (Fig 7).

6. CONCLUSIONS

It is shown in this theoretical study that mass transfer models can be used to predict the period needed to achieve a certain degree of PAH removal from soil by bioremediation. However, the biological degradation capacity must be sufficient to obtain mass transfer limited degradation of the contaminant. When this is the case, removal rates of PAHs are dictated by mass transfer processes. In model calculations on three different physical states of PAHs in soil matrices, the influence of key mass transfer parameters on the period needed for 99% PAH removal by bioremediation was investigated. In agreement with dissolution models (Rulkens and Bruning, 1995) it was found that mass transfer parameters, such as particle radius, water-solubility and sorption coefficients, indeed determine the efficiency of bioremediation under mass transfer limited conditions. However, these were model calculations on a theoretical basis. In order to give these considerations a practical use, more work is needed on the characterisation of the physical states of PAHs in soil matrices and validation of the proposed transfer models.

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THE NATURAL ATTENUATION OF CHLORINATED ETHENES AT DOVER AIR FORCE BASE, DELAWARE, USA.

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Keywords : aquifer, bioremediation, case history, chlorinated hydrocarbons, field test, groundwater clean-up, groundwater remediation, halogenated hydrocarbons, in-situ bioremediation, natural attenuation, trichloroethylene

SUMMARY

The RTDF Bioremediation Consortium investigation of the contamination of groundwater at Dover AFB with chlorinated ethenes has demonstrated the reductive dechlorination of PCE and TCE to cis-DCE and VC under anaerobic conditions maintained by methanogenisis in the most heavily contaminated area of the plume. The initial breakdown of PCE and TCE is followed by the oxidative destruction of cis-DCE and VC to carbon dioxide outside the anaerobic region of the plume.

Determination of the mass flux of chloroethenes through transects in the plume unambiguously proves that there is destruction of chloroethenes as the contamination migrates away from the source(s) area.

Contaminated Soil '98, Thomas Telford, London, 1998, 143–152

INTRODUCTION

The Remediation Technologies Development Forum (RTDF, a consortium of partners from industry, government agencies and academia). Bioremediation of Chlorinated Solvents Consortium is conducting an integrated laboratory and field study of the natural attenuation (intrinsic remediation) of chlorinated ethenes in the groundwater at Dover Air Force Base (AFB), Dover, Delaware, USA. The goals of the four year study are to demonstrate the effectiveness of natural attenuation, to develop a fundamental understanding of chlorinated solvent natural attenuation processes, and the development of protocols for implementing natural attenuation at other sites.

SITE CHARACTERISTICS

Dover Air Force Base is an operational USAF base located just to the south of Dover in Delaware. The Base is located on relatively flat ground with the shallowest groundwater located in the Columbia Formation, which is composed mainly of fine and coarse grained sands which range in thickness from 9m to 21m. The groundwater elevation of the Columbia aquifer ranges from approximately 4m MSL in the northern portion to less than 1m MSL near the St Jones River (Fig 1). Deeper aquifers within this region are protected by an extensive clay layer (Calvert Formation). The direction of groundwater flow is generally in the southerly direction, and because of the relatively shallow gradient (0.0008 to 0.0019), groundwater velocities are in the range 35 to 70 m per year.

GROUNDWATER CONTAMINATION

The plume of chlorinated hydrocarbons described in this paper is located within the West Management Unit of the Base and has been designated the Area 6 plume. The plume extends approximately 2600m from its northern to southern boundary and is 1000m across (east to west) at its widest point. It receives constituents from multiple sources of varying and unknown ages. These sources are confined to the aircraft maintenance facilities located to the north of US Highway 113. The main source contaminants associated with this plume are chlorinated solvents (perchloroethene, PCE and trichloroethene, TCE), however, there are also minor sources of petroleum hydrocarbon contamination within this region.

The groundwater chemistry has been characterised by the quarterly sampling of up to 50 boreholes since July 1995 with additional wells installed as required. The analysis has included measurement of all the volatile organic compounds including ethene and methane, a range of inorganic and biogeochemical parameters such as dissolved oxygen, nitrate/nitrite and sulphate/sulphide. All the information produced from the quarterly sampling has been stored in a geographical information database and the contour maps have been generated using Surfer® (Golden Software Inc.).

The aquifer was sampled at approximately 6m b.g.s. and 13m b.g.s. Based on the results obtained by this project and previous site investigations, the majority of the contaminants have been shown to be confined to the lower portion of the aquifer closest to the aquitard. Figures 2, 3, and 4 summarise the extent of the contamination by PCE and TCE and the daughter product *cis*-1,2-dichloroethene (cis-DCE) in the summer of 1996 in the deeper

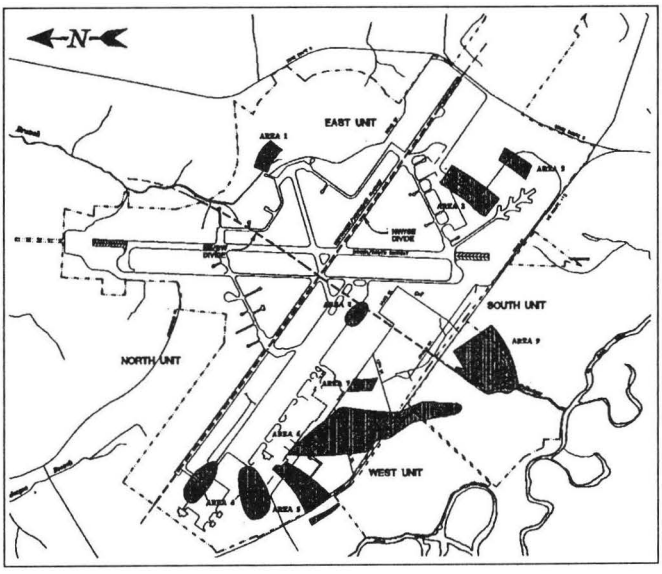

Figure 1 : Dover USAFB, Dover, Delaware, USA

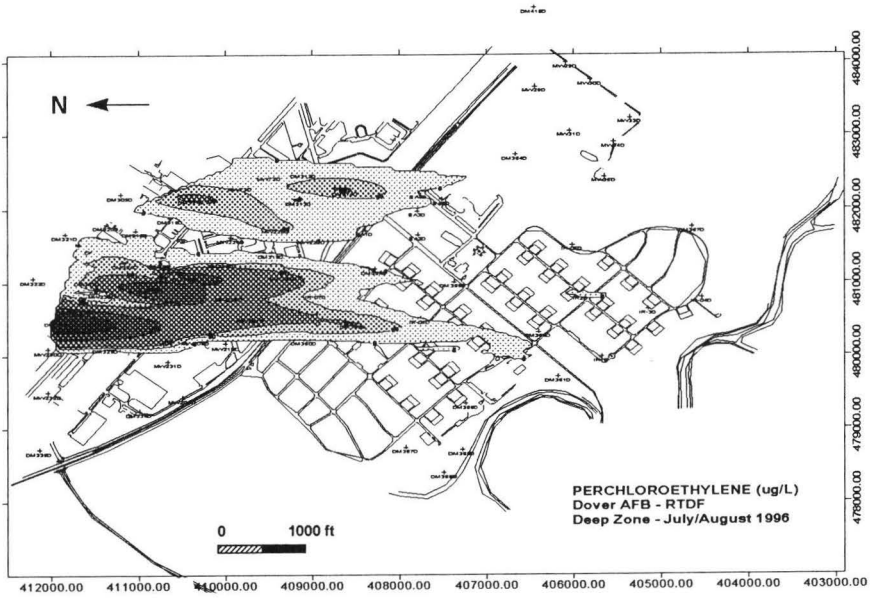

Figure 2 : PCE Contamination in the Deep Zone

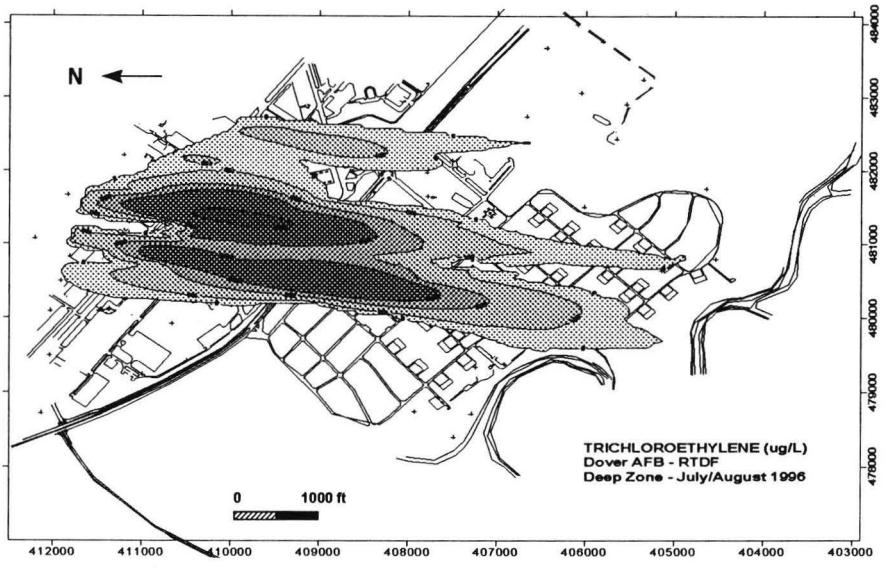

Figure 3 : TCE Contamination in the Deep Zone

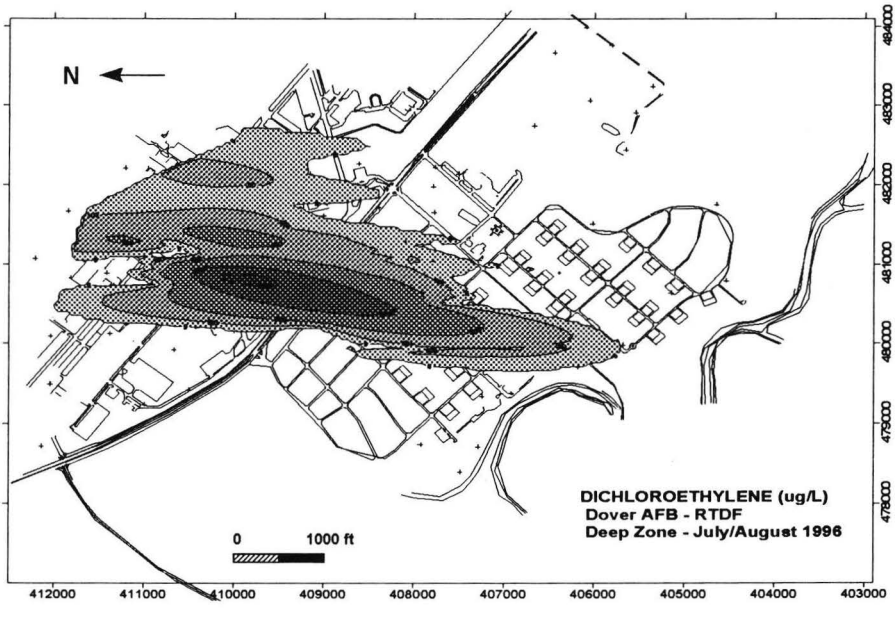

Figure 4 : cis-DCE Contamination in the Deep Zone

portion of the aquifer. The highest concentrations of PCE are located in an area to the north of US Highway 113 while the TCE contamination extends over a much larger area when compared to the PCE plume. The presence of several regions of high concentration of TCE probably reflects multiple sources.

The extent of groundwater contamination by *cis*-DCE overlaps the TCE plume and given that to the best of the knowledge of project was not used on the base is most likely to have been produced by the biotransformation of PCE and TCE. Further support for the biological origin of the DCE is based on the fact that only the *cis* isomer has been detected in the groundwater, whereas industrial produced DCE usually contains a mixture of the two isomers. Vinyl chloride (VC) was detected in a small area well within the area occupied by the *cis*-DCE plume. Ethene has also been detected in the groundwater, providing evidence for the complete dechlorination of the chlorinated ethenes.

BIOGEOCHEMISTRY

In addition to characterising the fate of the chlorinated ethenes, groundwater samples were also analysed for a range of constituents which can be used to help define the microbial ecology and biogeochemical processes responsible for the biotransformation process. In the vicinity of the plume the dissolved oxygen (DO) concentrations (Fig. 5) have been depleted to levels below 1 ppm while outside the contaminated area the concentration is close to the background level of 4 ppm. The measured concentrations of methane in the ground water display a pattern (Fig. 6) which is exactly opposite to that of the DO. Methane concentrations ranging from 50 ppb to greater than 700 ppb have been found within the contaminated area, while no methane is found outside the plume.

The concentration of hydrogen (H_2) dissolved in the ground water has been measured once in the field in 1996 and highest values (>30 nM/l) were found in the regions of highest contamination. The groundwater has also been analysed for the presence of nitrate and nitrite, reduced iron (Fe^{II}) and manganese, sulphate and sulphide. The results indicate that the deeper aquifer contains negligible levels of nitrate and sulphate with low and variable concentrations of reduced iron and sulphide.

These observations indicate that there is an anaerobic portion of the plume (DO < 1 ppm, methane > 300 ppb, H_2 > 5 nM/l), closest to the sources and in the region of highest PCE and TCE concentration followed, down stream, by an portion of the contaminant plume which is aerobic (Fig. 7). Based on the measurements of the various constituents of the redox couples it believed that methanogensis is the predominant electron transfer process responsible for sustaining the anaerobic zone.

CONCEPTUAL MODEL

A conceptual model has been developed to provide framework to help rationalise the information gathered on the plume. The key features of the model are :

- PCE, TCE and various hydrocarbons (e.g. jet fuel) entered the ground/groundwater from a variety of sources within the maintenance area over a period of time.

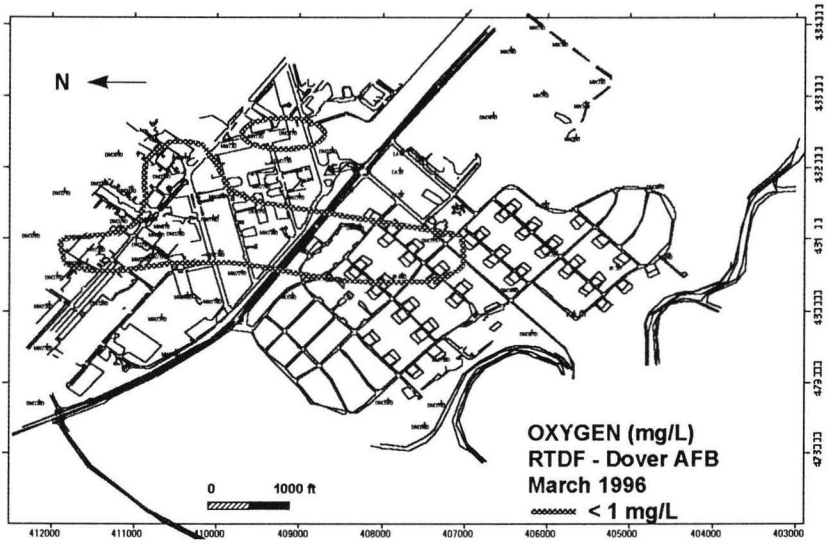

Figure 5 : Dissolved Oxygen in the Deep Zone

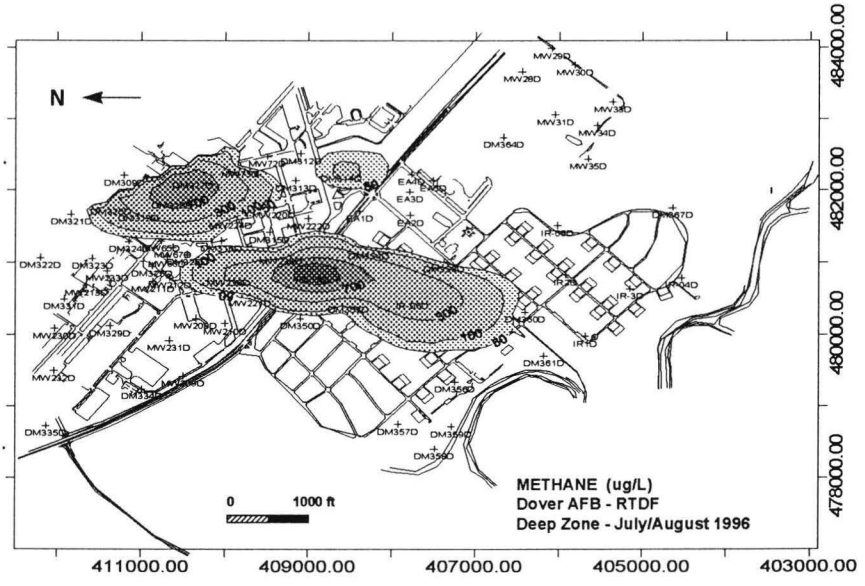

Figure 6 : Methane in the Deep Zone

- On entering the groundwater the PCE and TCE started to dissolve in the groundwater and any freephase material moved downwards to the bottom of the aquifer next to the aquitard. Once in the groundwater the dissolved PCE and TCE together with any DNAPL migrated in the general direction of the groundwater flow (south towards the St Jones River)

- The hydrocarbon contamination tended to form LNAPLs on top of the aquifer together with a dissolved plume in the groundwater. Over time the plume of dissolved hydrocarbons mixed with contaminant plumes containing PCE and TCE.

- Once dissolved in the aquifer the hydrocarbons became readily available as a carbon source for the microbiological population and underwent oxidative breakdown to carbon dioxide and water, consuming the DO as the electron acceptor and so generating anaerobic conditions, particularly in the deeper groundwater.

- The anaerobic conditions in the deeper region created the environment for the microbiological consortium to breakdown PCE and TCE by reductive dehalogenation. This process occurs either as a fortuitous cometabolic process or one in which the chlorinated species is the main electron acceptor i.e. it is involved in the anaerobic respiration / energy production.

- The dissolved hydrogen concentrations (Ref 1) together with the methane measurements support the view that the predominant microbiological process in the anaerobic region is methanogenisis

- Alternative pathways (Fig. 8) for the breakdown of cis-DCE and VC open up as the chemicals migrate out of the anaerobic zone into the aerobic aquifer. These alternative mechanism lead to the rapid oxidative destruction of these particular chloroethenes and offer an explanation as to why significant quantities of these chemicals are not found down gradient of the TCE but are predominantly (especially the VC) located within the anaerobic / most heavily contaminated region of the plume.

TRANSECT STUDY

The overall objective of the transect study was to collect sufficient data to determine the mass flux of chloroethenes in the plume and to use this data to clearly show the overall destruction of chloroethenes within the plume.

To generate the data samples of groundwater were collected in the spring of 1997 at various depths using a Stratoprobe® along three transects at right angles to the main axis of the plume. The transect locations were selected based on the chloroethenes distribution in the deeper region of the aquifer downgradient of the source area (Fig. 9). They extend beyond the known transverse limits of the chloroethene plume.

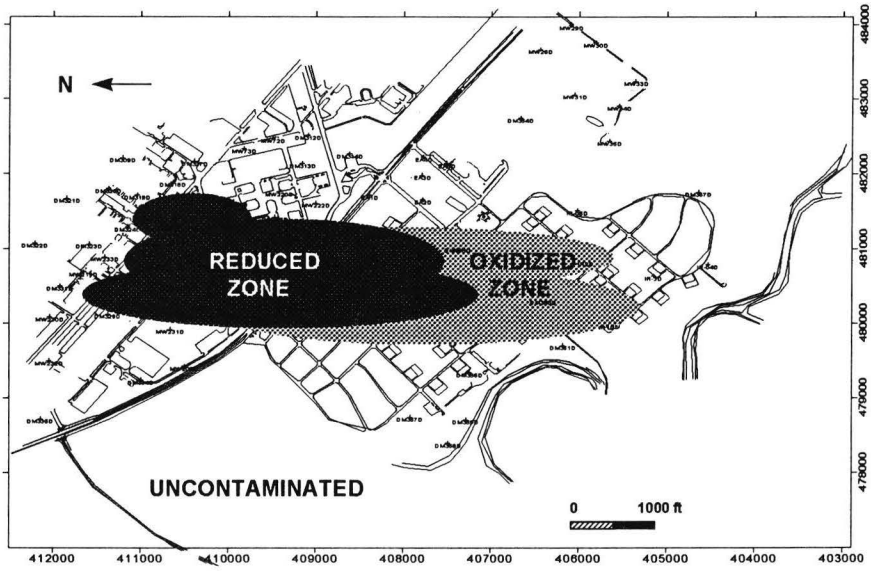

Figure 7 : Redox in the Deep Zone

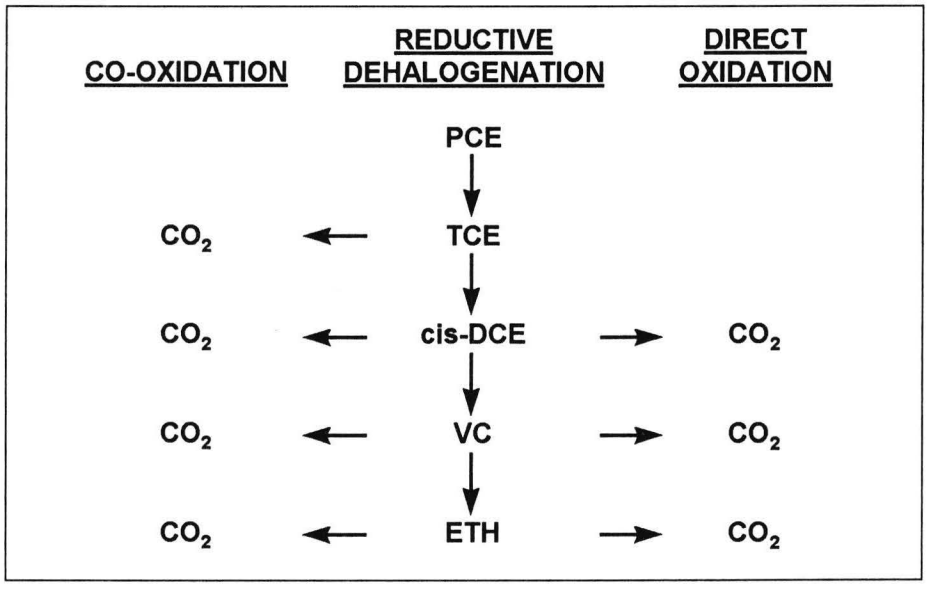

Figure 8 : Pathways for Biological Degradation of Chloroethenes

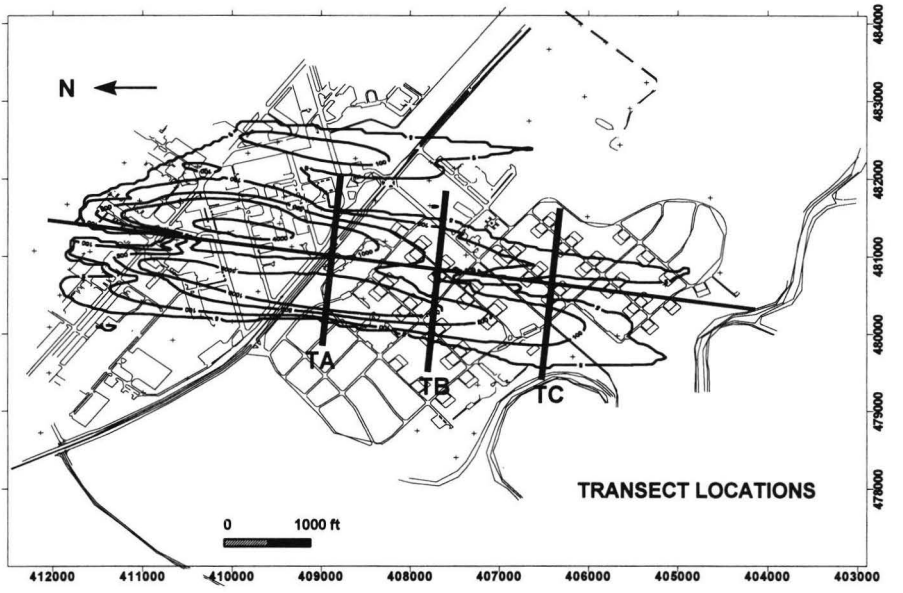

Figure 9 : Location of Transects

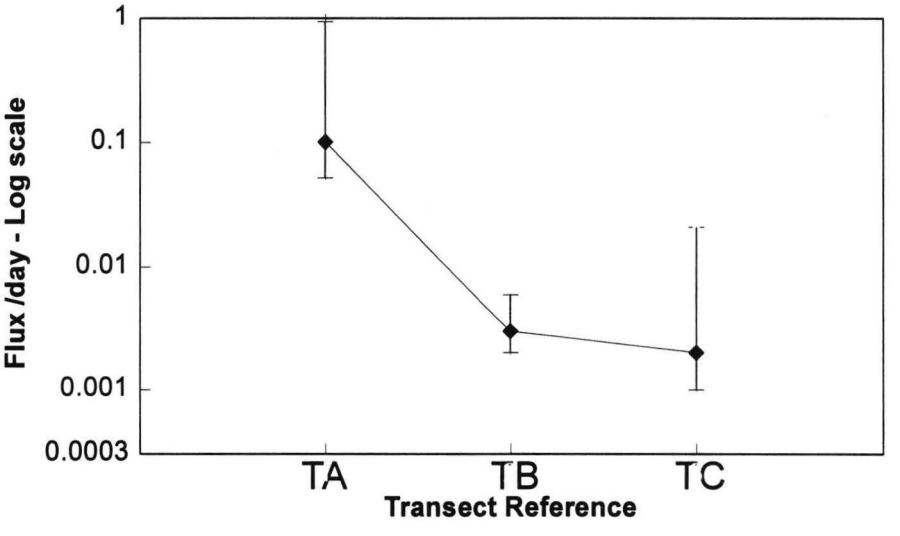

Figure 10 : Mole Flux / day of Chloroethenes by Transect

At each sample position the hydraulic conductivity (k) was determined using the method described by J Wilson (Ref 2) and a sample of groundwater was taken for laboratory analysis to determine the concentration of the chloroethenes (c). The hydraulic gradient (i) was derived from piezometer reading across the area of interest.

The total mole flux of chloroethenes (M_T) through a transect was calculated from :

$$M_T = \int_A K_P \, i_P \, c_P \, dA_P$$

and an estimate of the error involved in the integral for each transect was obtained by deriving the mean value and variance for $K_P \, i_P \, c_P$ based on a lognormal distribution for each transect. The results are contained in Figure 10 and clearly show a destruction of chloroethenes as the contamination moves away from the sources.

CONCLUSIONS

The field work has demonstrated the reductive dechlorination of PCE and TCE to cis-DCE and VC under anaerobic conditions maintained by methanogenisis in the most heavy contaminated area of the plume followed by the oxidative destruction of cis-DCE and VC to carbon dioxide outside the anaerobic region of the plume.

Determination of the mass flux of chloroethenes through transects in the plume unambiguously proves that there is destruction of chloroethenes as the contamination migrates away from the source(s) area.

Natural attenuation processes provide protection of the prime environmental target (the St. Jones River) by conversion of the chloroethenes to benign compounds i.e. chloride salts, ethene and carbon dioxide.

ACKNOWLEDGEMENTS

The work described in this paper is a collaborative project by the RTDF Bioremediation of Chlorinated Solvents Consortium. The input of all members of the Consortium is acknowledged and the authors would like to express their thanks to everyone involved in the project.

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HYPER-SPECTRAL REMOTE SENSING OF THE SPREAD OF SOIL CONTAMINANTS FROM LANDFILL SITES

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Key words: Landfill gas, landfill leachate, vegetation, environmental impact, monitoring

SUMMARY
Recent improvements in the spatial and spectral resolutions of remote sensing imaging instruments have increased vastly their ability to detect subtle variations in the health of vegetation and in the soil in which it is growing. This capability, coupled with the unique ability of remote sensing data to produce synoptic maps of a land surface, make them a potentially powerful tool for monitoring the spread of contaminants within a soil-body. The aims of this paper are to inform the contaminated soils community of these advances and describe our ongoing research into methods for exploiting these data sources for monitoring soil contamination, in particular around landfill sites.

KURZFASSUNG
Kürzliche Verbesserungen des räumlichen und spektralen Auflösungsvermögens von Fernerkundungsinstrumenten haben deren Fähigkeit geringe Variationen in dem Zustand von Vegetation und zugehörigem Boden zu entdecken erheblich verbessert. Diese Fähigkeit, zusammen mit der einzigartigen Verwendbarkeit von Fernerkundungsdaten übersichtliche Karten der Erdoberfläche zu produzieren, machen sie zu einem wirksamen Werkzeug zur Überwachung der Ausbreitung von Bodenverunreinigungen. Das Ziel dieser Veröffentlichung ist es Bodenkundlern von diesen Verbesserungen zu berichten und unsere gegenwärtigen Forschungsergebnisse über die Methoden der Datenverwendung für die Überwachung von Bodenverunreinigungen besonders in Deponien zu beschreiben.

RÉSUMÉ
Des améliorations récentes au résolution des instruments de télédetection ont augmenté vastement leure capacité de découvrir les variations de la santé de végétation et du sol dans lequel il se trouve. Cette faculté, couplé avec la capacité unique des data de télédetection de produire des cartes synoptique d'une surface de terre, les rendre un outil très fort pour suivi le pollution de sol. Ce papier aspire à informer le communauté de pollution de sol de cettes avances et décrit nos recherches courants aux methodes pour exploiter cettes sources de data.

Contaminated Soil '98, Thomas Telford, London, 1998, 153–161

1. INTRODUCTION

Whereas the use of aerial photography and stereo-photography have been familiar tools to environmental scientists, managers and engineers for many years, the use of digital imagery from air- or space-borne instruments has gained currency only recently in these fields. Digital images are made up of discrete picture elements or "pixels". The image is recorded electronically in the form of a series of binary numbers which represent the the level of reflected radiation from the land surface being imaged.

The most common form of this technology used for land-based applications is the so-called "multi-spectral" imager. These instruments provide images in a relatively-small number (typically between two and twelve) of relatively-wide spectral wavebands, from which crude but reliable measures of the level of vegetation at each point in the image can be deduced. This has proved useful in a limited way, when operated from aircraft, for directing in situ monitoring of soil contamination due to the migration of methane and leachate around landfill sites.

Although such instruments have been operated from satellites for over twenty-five years, the images they produce have, until very recently, been further limited in their utility for contaminated soil monitoring by their poor spatial resolution: in these data, the radiation from areas at best 30m across have been averaged to give a single reading. This is clearly insufficient for studying the often small scale variations in contamination that occur near a landfill site.

Recently, both the spatial and spectral resolution of data have improved greatly. Satellite data is now available with spatial resolution of less than 5m whereas aircraft data is capable of 1m resolution. So-called "hyper-spectral" data is now also available. This takes readings in several hundred very narrow wavebands across the spectrum and thus provides a quasi-continuous spectrum of reflected radiation. Current satellite instruments have one or other of these attributes, while airborne instruments are available which have both. Where the improved spatial resolution will provide much closer scrutiny of the small-scale variations in contamination, the hyper-spectral capabilities of these instruments will provide much more subtle analyses of the health of vegetation and the nature of soils, and thus give a much more accurate indication of the level and nature of their contamination. The exploitation of these capabilities provides the next major challenge for the land surface remote sensing research community.

2. PREVIOUS WORK

A number of research projects have investigated the potential for using remote sensing data to monitor the evolution of contaminated land and landfill sites and in particular their environmental impact. At the simplest level, these have advocated the use of black and white or colour aerial photography (e.g. Rugge and Ahlert, 1992; Lyon, 1987; Airola and Kosson, 1989) and photogrammetry (e.g. Warner, 1994). Such an approach provides a relatively-low cost method of identifying gross-scale changes in the land cover on and around a site, the structure of the site itself, and can give

topographic information useful for computing available void space in a landfill and assessing geotechnical stability.

On the next level, many studies have assessed the use of multi-spectral data. These developed typically from previous work which used remote sensing to identify geological and hydrogeological features (e.g. Vincent, 1994; Johnson et al., 1993). It is aimed at identifying areas of vegetation stress using the vegetation index or classification methods described above. The stress acts as a tracer for migrating gas and leachate within the soils, since contaminants in these migrants are amongst the causes of changes in vegetative health. Most work has been carried out in the area of hazardous waste sites (e.g. Stohr et al., 1987) although more recent work has been carried out on domestic waste sites (Jones and Elgy, 1994; Griffiths et al., 1996).

In Situ Survey	Remote Sensing Survey
Disadvantages • Data at fixed points in space - limited data on overall spatial distribution • Data at fixed points in time - limited data on overall temporal variations • Difficulty of access	**Disadvantages** • May be unreliable due to cloud cover • Atmospheric distortion of data • Requires in situ data to confirm and quantify presence of gas • Surface data only
Advantages • Quantitative, reliable measurements of gas or leachate concentration • Measures vertical distribution within soil	**Advantages** • Non-intrusive data acquistion • Synoptic coverage • Holistic view • Low marginal costs

Table 1: Summary of the advantages and disadvantages of in situ and remote sensing survey methods (after Jones and Elgy, 1994)

As stressed by Jones (1991) and Hopper (1996), remote sensing is not envisaged in this respect as a substitute for in situ borehole sampling methods. Rather, the approach adopted is to integrate both techniques to optimise their individual advantages. Table 1 summarises the nature of this integration. Many difficulties have been identified in the use of this method. At the root of these is the complexity of the context within which the contaminants are moving. Plant type, soil characteristics and hydro-geology (which determines pathways for migrating gas and leachate) will all cause a very high level of variation across the site. Mis-management, the extent to which land is subject to other stresses (such as being driven over repeatedly) and other anthropogenic effects will also confuse the issue. Clearly the remote sensing approach described will operate best when the following factors are present (adapted from Jones and Elgy, 1994):

- high concentrations of gas or leachate
- homogeneous vegetation cover
- vegetation species susceptible to damage by landfill-derived contaminants
- consistency of other variables, such as soil characteristics

Within this approach, it is possible to identify four general levels of vegetation stress identifiable from multi-spectral data (Murtha, 1976):

- complete defoliation
- partial defoliation
- spectral changes in the visible wavelength range (i.e. colour change)
- spectral changes in the near infra-red wavelength range (i.e. no visible change)

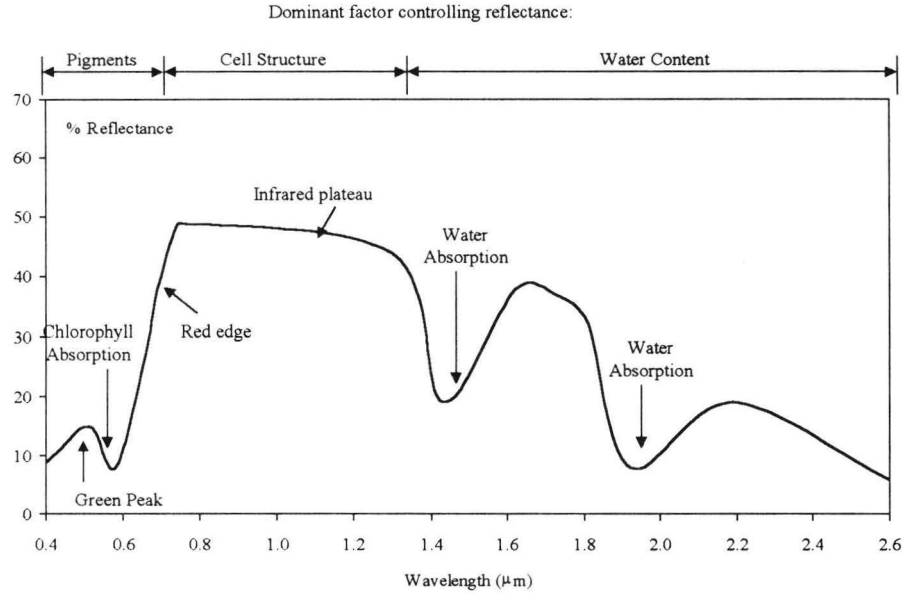

Figure 1: A typical electromagnetic reflectance spectrum for vegetation, showing the sources of the variation in reflectance with wavelength (after Griffiths et al., 1996)

These variations arise within the context of the reflectance spectrum of a typical healthy plant, as shown in Fig. 1. As a result, Gausman and Quisenberry (1990) have identified three wavebands useful in the detection of vegetation stress:

- the main chlorophyll absorption line at 0.50-0.75 μm
- the region of high reflectance at 0.75-1.35 μm
- the extended region of absorption in the spectrum of water at 1.35-2.5 μm

These wavebands are available in typical airborne instruments which have been used in this type of research. Most common is the Airborne Thematic Mapper, which has twelve channels, of which three have been specifically designed to monitor variations in the characteristics of plants in the wavebands listed above.
More recent work has begun to develop the possibility of using hyper-spectral data to identify contaminants in soils and the effects they have on vegetative health and reflectance spectra. In particular, Jago and Curran (1995, 1996, 1997) have carried out extensive studies aiming to characterize the relationship between chlorophyll concentration, contamination, and the shape and position of the chlorophyll red-edge in spectra of plants recorded from both hand-held, ground-based spectrometers, and airborne instruments such as CASI using a set of fourteen bands chosen to best characterize the red-edge. This work has found a well-correlated relationship between these parameters which implies that the use of hyper-spectral data can provide a very significant improvement in the contaminant-monitoring capabilities of remote sensing data over that provided by multi-spectral data.

3. CURRENT WORK

The current work aims to investigate in more detail the application of hyper-spectral remote sensing to the monitoring of vegetation stress and contaminant migration around landfill sites, building on recent work in the U.K by Jones and Elgy (1994), Griffiths et al. (1996) and Jago and Curran (1997). Because of a delay in data provision, due to changes in the pre-processing systems of the data provider (the U.K. Natural Environment Research Council) final results are not currently available. The planned methodology is described here to demonstrate the potential advances which this research will provide.

The site currently under investigation in this study is at Barkip, to the south of Glasgow in Western Scotland. It is located within relatively homogeneous hydro-geological and land-cover contexts. The project uses data from the U.K. Natural Environment Research Council's Annual Airborne Remote Sensing Campaign, which provides Compact Airborne Imaging Spectrometer (CASI) imagery of the landfill sites. Data is taken in the spectral mode, such that the whole array of spectral channels is used in the data recording. This provides quasi-continuous spectra in pixels at a spatial resolution of 2-3 metres. Various methods of analysis are carried out to ascertain the improvements available using the most advanced of those techniques. Classical measurements of vegetation indices will be attained using averaged pixel intensities from the CASI bands within the ranges traditionally used for this parameter, as described above. These will give, at the simplest level, an indication of the vegetative health around the landfill sites and provide a benchmark against which more sophisticated techniques can be measured.

The next level of analysis will follow that described by Jago and Curran (1997), who fitted the shape of the red edge to an algebraic function, and thus objectively defined its position. These researchers then found a strong relationship between this position, and the concentration of chlorophyll in plant samples. The latter is known to have a strong correlation with the level of contamination in the soil in which the plant is growing.

Finally, an approach will be adopted using artificial neural networks. This will be based on rules of thumb describing changes in the spectrum due to levels of contamination and other factors such as soil moisture content, texture, pH and TOC, and plant type and maturity. The rules of thumb will be developed from subjective analyses of the entire spectrum of each pixel. Using this approach, the intention is that variations in the spectra due to contaminant presence can be distinguished from those due to other factors. The extent to which this can be achieved will be the major focus of future investigations.

In order to determine the situation in each pixel thus analysed, a number of soil and vegetation samples will be taken from the sites simultaneously with the remote sensing overflights. These will be analysed for soil characteristics (pH, moisture content, texture, TOC) and plant characteristics (species fractions, maturity, chlorophyll concentration, leaf area index) as well as contaminant levels in both soil and plants (methane, heavy metals, PAH's). These in situ results will then be compared to the remote sensing data in order to develop the ANN described above.

4. COST-EFFECTIVENESS AND COMMERCIALISATION

Landfill monitoring currently falls somewhat between the two stools of airborne and satellite remote sensing. Its data requirements can be summarised as follows:

- Spatial Resolution: Of the order of 1 m, although <5 m is acceptable
- Spectral Resolution: Quasi-continuous spectrum
- Temporal Resolution: One overflight each several days

The required temporal resolution does not pose a problem for satellite based sensors. Typically these return to monitor the same area of land once a fortnight. In this time, the situation at any given landfill site is likely to have changed only incrementally, and this change can thus be monitored effectively from a satellite-borne sensor. However, although satellite data are now becoming available which have spatial resolutions of less than 5 metres, as required for landfill monitoring, these are either monochromatic, or available in only two or three separate wavebands, and thus are severely limited in terms of their spectral resolution. Conversely, satellite data are available with hyper-spectral resolution from the new Australian ARIES-1 satellite (and a number of satellites to be launched in the near future), but with a spatial resolution of greater than 10m per pixel. Thus there is not presently a satellite borne sensor ideal for landfill site monitoring.

The potential for the development of such instruments is, however, high. Developments in the 1990's have seen instruments with greatly improved spatial or spectral resolutions. It seems inevitable therefore that a combination of these attributes in a satellite borne instrument is likely within the next decade. The major technical problem to overcome is that of downloading the massive amount of information from such a system. For example, increasing spatial resolution from 30m per pixel to 3m per pixel, increases the amount of data gathered one-hundredfold. Increasing the

spectral resolution from five channels to one hundred results in a twenty-fold increase in data. Combining these two implies two thousand times the amount of data of current instruments such as the Landsat Thematic Mapper.

Airborne sensors, on the other hand, such as CASI and AVIRIS, do fit the three-fold resolution requirements as listed above. From the point of view of cost, however, they are at a severe disadvantage in comparison with satellite data. The latter are provided at relatively-low cost by commercial companies since the satellite is constantly producing a stream of data which can be received by any of several designated receiving stations around the world. The acquisition of airborne data, however, requires the rental of the instrument and its (extensive) associated hardware. This usually has to include rental of the plane on which it is mounted, since the aircraft must have the requisite attributes to house the instrument. Skilled staff are required to operate the instrument whilst it is in flight. Costs are also incurred in gaining air clearance, runway slots and Civil Aviation Authority authorisation. As a result, this process is limited to large scale projects, and government-funded bodies such as research councils and the U.K. Environment Agency. The costs for a small or medium sized landfill operator in hiring such a craft would be likely to be prohibitive.

A potential solution lies in the development of low cost, easy to operate hyper-spectral instruments. An example of this is the VIFIS instrument which is currently being developed at the University of Dundee in Scotland (Sun and Anderson, 1994). The availability of such an instrument at a fraction of the cost of instruments such as CASI and AVIRIS suggests that it may become possible for landfill managers, individually or in groups to purchase such instruments and thus monitor the environmental impacts of their sites. More likely is the scenario that environmental protection agencies will carry out overflights of sites on an operational basis and use the information thus gained in the guidance and control of landfill operators' activities. The Environment Agency of England and Wales already possess a CASI system. The development of algorithms that will allow them to gain meaningful information from its operational use are now required to justify that use. Environmental protection agencies in smaller countries or regions, such as the Scottish Environmental Protection Agency, would find it harder to justify the outlay for a CASI system. The development of standardised, cost-efficient processing systems for instruments such as VIFIS, or the availability of satellite data combining high spatial and spectral resolution, are likely to be necessary before agencies in these areas can begin operational remote sensing monitoring of landfill sites. However, as stated above, such a scenario is likely within the first decade of the 21st century.

The viability of remote sensing data as a commercial product is not in doubt. Numerous companies have grown up in the last two decades dedicated to this product range, and are currently flourishing. Successful areas of commercial exploitation include weather forecasting (for general and specific needs), geological prospecting, precision farming, land-use mapping and coastal vessel monitoring (of particular interest to customs and excise offices). Current work is aimed at developing the algorithms whose development has been described in this paper into commercially-

marketable services that will significantly enhance the environmental monitoring capabilities of the landfill and contaminated land management communities.

5. CONCLUSIONS

Details have been presented of completed and ongoing research into the application to land contamination monitoring of remote sensing data from both airborne and spaceborne instruments. Currently, methodologies developed to an operational level are able to use multi-spectral data to identify relatively crude measures of vegetative health, which can be used to direct in situ sampling and thus increase its efficiency and efficacy. Recent work studying the hyper-spectral data produced by imaging spectrometers has demonstrated that the more subtle variations distinguished in this data will improve the added-value to the contaminated soils community from remote sensing data. Current work has been described which aims to develop methodologies based on artificial neural networks which will be able to more fully distinguish variations in vegetative health caused by soil contamination from that caused by other factors such as changes in soil characteristics and plant phenology over a site.

The next decade offers exciting advances in this field, as low-cost airborne systems, and spaceborne systems of sufficiently high spatial and spectral resolution come on-line, and processing algorithms such as those described here are developed in parallel.

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A SYSTEMATIC APPROACH TO THE INVESTIGATION OF PESTICIDE (HCH) CONTAMINATIONS IN URBAN-INDUSTRIAL AREAS OF DEVELOPING COUNTRIES - THE CASE OF RIO DE JANEIRO METROPOLITAN AREA, BRAZIL

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Key words: contaminated sites, pesticide (HCH), soil and groundwater contamination, environmental policy instruments

SUMMARY
The contamination of soil and groundwater by residues of the hexachlorcyclohexane(HCH) pesticide production is a widespread problem in urban and rural regions of Brazil. The investigation of the Cidade dos Meninos site in the metropolitan area of Rio de Janeiro reveals the elevated risk potential of these sites and emphasises the urgency to seek technical and political-legal solutions for the problem in Brazil.

KURZFASSUNG
Die unsachgemäße Entsorgung von Rückständen der Hexachlorcyclohexan (HCH) Pestizid Produktion verursachte zahlreiche Boden- und Grundwasserkontaminationen in städtischen und ländlichen Regionen Brasiliens. Die Untersuchung einer dieser Altlasten in der Cidade dos Meninos im Großraum von Rio de Janeiro zeigt das Gefährdungspotential und die Notwendigkeit auf, technische und politisch-rechtliche Lösungen für diesen Altlastentyp zu erarbeiten.

RÉSUMÉ
La contamination des sols et des eaux souterrains par résidus provoqués par la production de hexachlorecyclohexane (HCH) c'est un problème fréquemment rencontré dans les régions rurales et urbaines du Brésil. La recherche realisé dans la "Cidade dos Meninos", située dans la région métropolitaine de Rio de Janeiro, montre le risque potentiel très grand de ces locaux et montre l'urgence de trouver des solutions techniques et politiques - legaux pour ces problèmes au Brésil.

Contaminated Soil '98, Thomas Telford, London, 1998, 163–171

1. INTRODUCTION

The problem of soil contamination resulting from the production and disposal of pesticides, in particular hexachlorocyclohexane (HCH) and related contaminants is known from different sites in Brazil. The first systematic approach concerning the investigation and remediation of these contamination in former HCH production and disposal sites has been elaborated during a joint venture project between the State Environmental Agencies of Rio de Janeiro (FEEMA), São Paulo (CETESB) and Porto Alegre (FEPAM), being iniciated by the Project Network "CIP" of the Technical Co-operation between Brazil and Germany under sponsorship of the German Association for Technical Co-operation (Deutsche Gesellschaft fur Technische Zusammenarbeit, GTZ).

In 1996 the three State Environmental Agencies carried out an investigation in three different pesticide contaminated sites with the purpose to elaborate a data base for risk assessment and remediation planning and at the same time to technically qualify the environmental agencies in the field of contaminated site investigation.

This paper will focus on a former HCH production site in the metropolitan area of Rio de Janeiro. The industrial installations were deactivated after an 11 year production period. From the beginning on, HCH residues were abandoned on the terrain without any sufficient means of safety and alert concerning the risks of the substances involved. Health problems of the population were reported since then and few isolated toxicological studies were carried out to determine the exact contamination paths, which were believed to be the direct contact with the contaminants. However no unambiguous results were obtained.

At the end of 1995 a remedial action consisting in mixing HCH residues with a blend of calcium and magnesiumoxide (CaO/MgO) was carried out in order to degrade HCH to 1,2,4 trichlorbenzene (TCB) in situ. The "lime remediation" was executed without any precautions and containment measures regarding TCB and other metabolites.

2.METHODOLOGY

In order to characterise the contamination at "Cidade dos Meninos"(19 million m^2) the investigation was concentrated on the former production site (13,000 m^2), as well as on a survey of secondary focuses all over the area (Fig. 1).

To investigate the qualitative and quantitative parameters of the contamination and the propagation possibilities in the soil and groundwater, in the Central Area of the Factory (ACF + CM 06) the following investigations were carried out (Fig. 2,3):

- -collection of samples in small barrels from 36 to 50mm (percussion probe) until groundwater level at the local CM 02 up to 09
- -description of the geological profile in the sampling holes
- -PID (photo ionisation detector) tests in borehole soil samples
- -Beilstein tests on superficial soil samples (incineration of chlororganic pesticides on a copper wire, giving a green flame)
- -register of the groundwater level

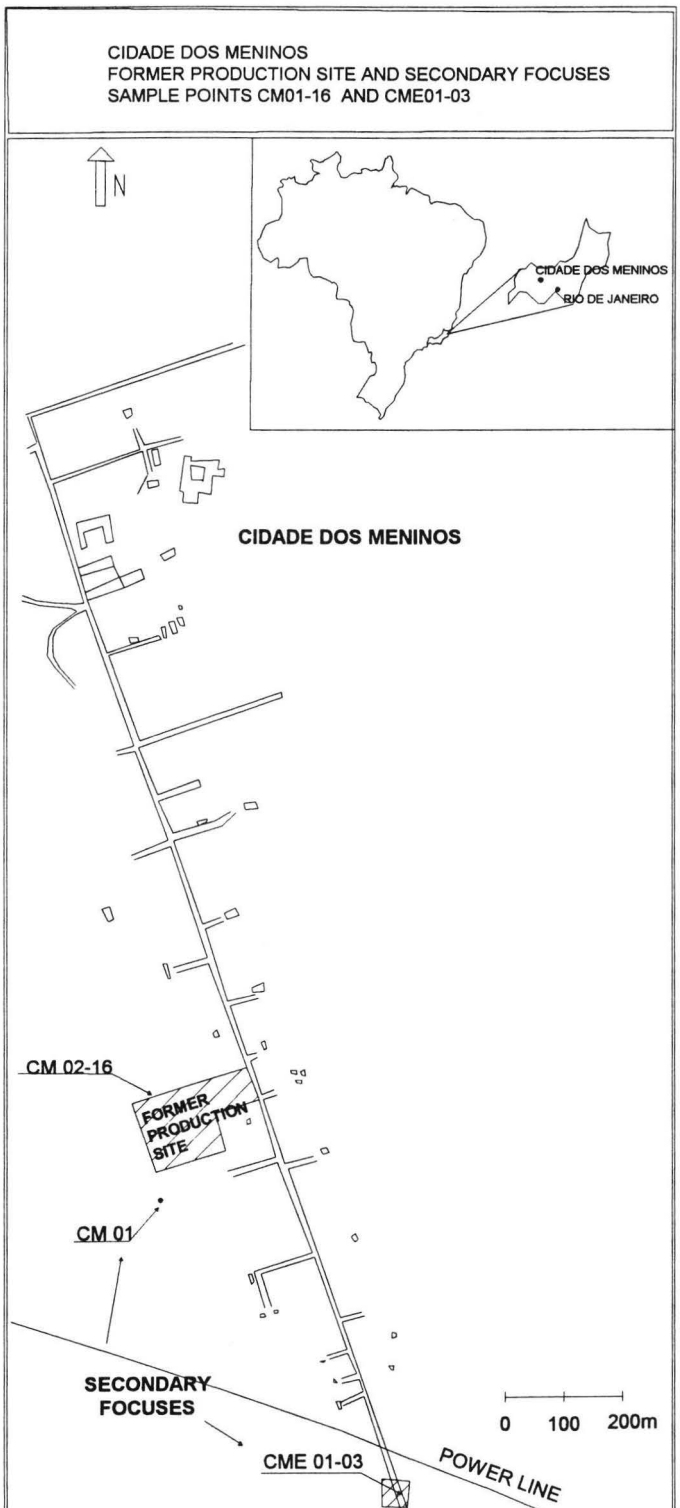

CIDADE DOS MENINOS
FORMER PRODUCTION SITE AND SECONDARY FOCUSES
SAMPLE POINTS CM01-16 AND CME01-03
N
CIDADE DOS MENINOS
RIO DE JANEIRO
CIDADE DOS MENINOS
CM 02-16
FORMER PRODUCTION SITE
CM 01
SECONDARY FOCUSES
CME 01-03
POWER LINE
0 100 200m

Figure 1

- collection of superficial samples (0-30cm) in the areas not visibly affected by the lime remediation in the production area of the factory (AF) (CM 10 up to 16)

Regional reconnaissance studies were used for the identification of secondary focuses. By multitemporal aerial photograph analysis (1976,1989,1996), based on the comparison of the photos, changes in suspected areas can indicate locals of waste disposal. The verification of the results of the photos 1989/96 was made by visits in the field and through shallow surveys (down to 50 cm depth). Interviews were also made with the neighbourhood population regarding other probable places of disposal of residues.

3. ANALYTIC METHODS

The soil samples were homogenised, weighed (10 grams), mixed with sodium sulphate anidro and extracted with 100 n-hexane ml for analysis of residues, in ultra-sound for 20 minutes.

The organic extract was filtered in sodium sulphate. The extracts were analysed by gaschromatography with electron detector capture and packed column (1,5% QF-1 + 1,95% OV-17). US EPA standards were used for identification and quantification of the samples. External calibration was used. Blanks were prepared in the same conditions as the samples to verify interference.

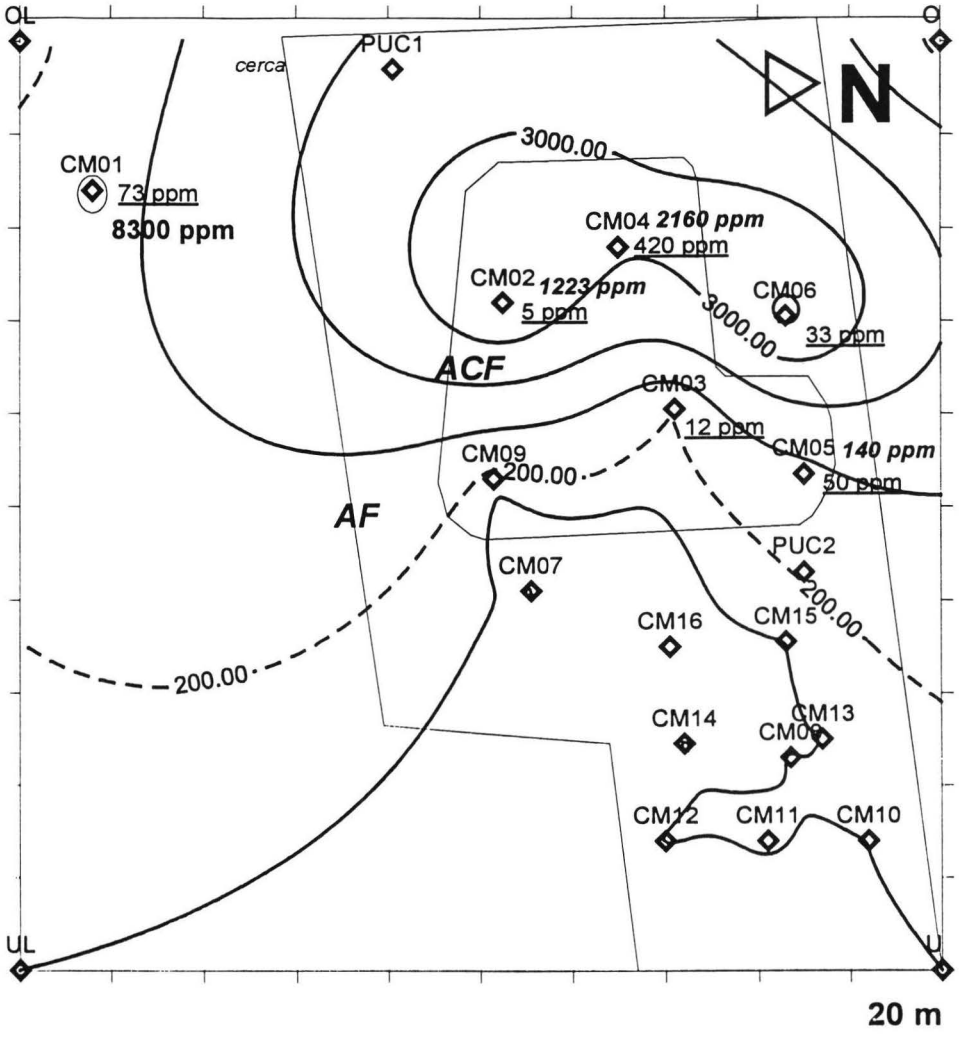
The sample humidity was determined in agreement with FEEMA's method and the results were expressed in dry weight.

The detection limits obtained are 0,1 μg/g for alpha, beta, gamma and delta HCH, individually.

4.RESULTS

In the area of the production site (AF), the soil profile consists basically of three individual layers of different thickness and variable depths. The geological sequence of the layers as shown in Tab. 1, was found in all the survey profiles. The reworked topsoil corresponds to the layer of application of lime.

The central part of the former production site (ACF) which corresponds to the zone of application of lime, was investigated in CM 02-06 and CM 09. The CM 06 borehole is outside the lime application zone. On the surface (depth: 0-70cm) the hot spot contamination of HCH forms a kidney-like belt between CM 02 and CM 06, with lower values in the East between CM 09 and CM 05 (Fig. 2). The picture is reflected in the contents of total HCH of the sandy and clayey layers (depth 70-170 cm) (Fig. 3). The vertical propagation of HCH reaches down to the clay layer in CM 02, 03 and 05.



Underline: gamma-HCH (other points not sampled)

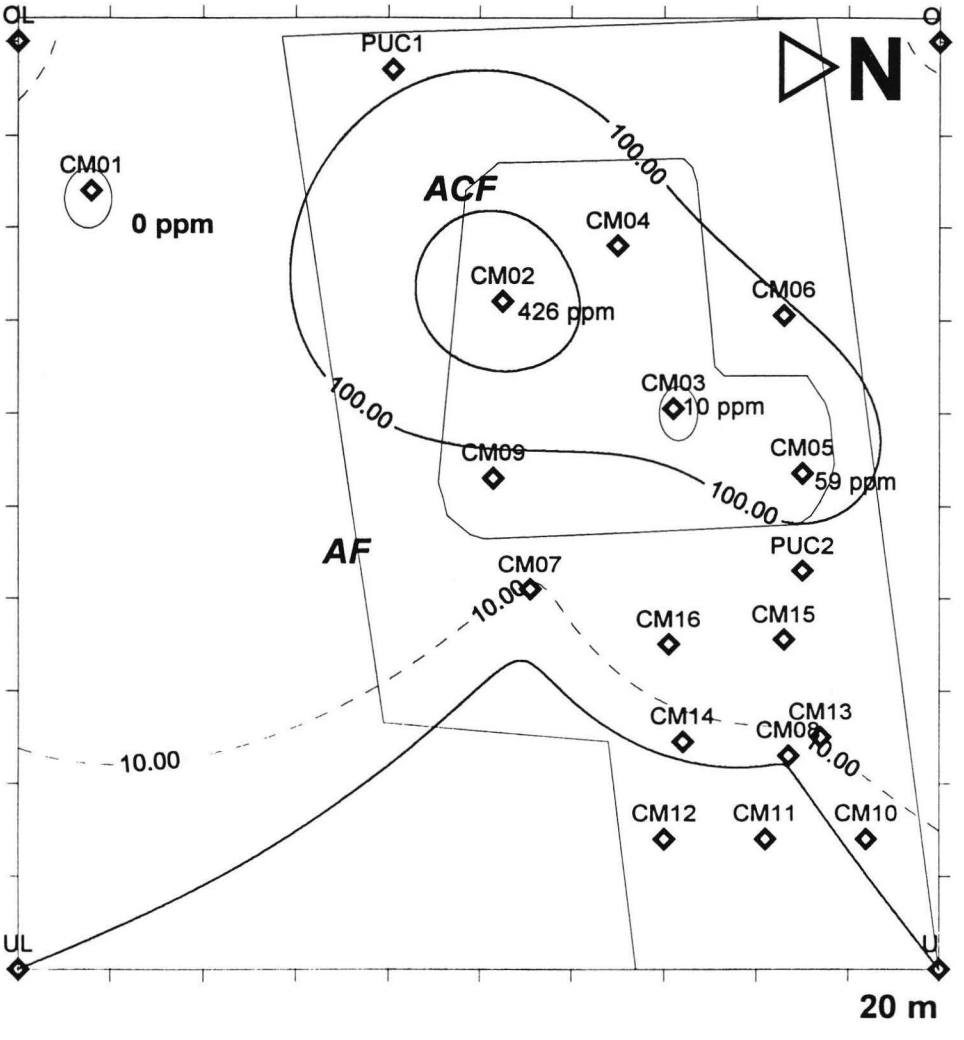
Bold italic: TCB (other points not sampled)

CIDADE DOS MENINOS
Former production site

August 1996

HCH total/ppm
depth: 0-70 cm

Figure 2



CIDADE DOS MENINOS
Former production site

August 1996

HCH total/ppm
depth: 70-170 cm

Figure 3

Table 1 Simplified description of the geological profile and PID measurements of the horizons sampled in the survey boreholes

Depth (m) Description	Thickness	Description
0-70 cm	50-80 cm	reworked topsoil, visibly polluted (PID: up to 80 ppm), sand blended with parts of pure HCH
70-200 cm	100-150cm	medium-coarse sand with feldspatic grains, yellow-reddened oxidised in the oscillation zone of the watertable and grey in the saturated zone (PID > and < 1 ppm)
> 200 cm	> 100 cm	plastic grey-white clay with red stains (PID < 1 ppm)

In ACF trichlorbenzene (TCB) was found in high concentrations only restricted to the superficial horizon (CM 02, 04 and 05) of the area of the "lime remediation." A propagation of TCB to lower levels was not observed (Fig. 2).

The distribution of gamma HCH in the superficial horizon does not reveal a systematic relationship with the contents of total HCH (Fig. 2).

The total volume of soil contaminated by HCH with contents >100 ppm until a depth of 1.7 m is approximately 15.000 m^3, corresponding to approximately 33 tons of total HCH (Tab. 2). This calculation was based on the interpolation of isoconcentration lines of Fig. 2 and 3 which represents a rough approach to the real distribution of the substances.

Table 2 Calculation of the volume of HCH-contaminated soil and the amount of HCH in the soil in dependence of depth and concentration range of total HCH; method: calculation of cells based on soil density of 2 g/cm^3 and 20% of humidity

	Conc. range (ppm)	Conc.average (ppm)	Volume (m^3)	HCH total (metric tons)
Depth(m)				
0-0.7	3000-4000	3500	1995	11.17
0-0.7	2000-3000	2500	4130	16.51
0-0.7	1000-2000	1500	1260	3.24
0.7-1.7	100-200	150	7700	1.73
Total			15085	32.65

Outside ACF in the east side of AF (CM 07, 08, 10-16), the HCH contents vary between 0.2 and 5.15 ppm in the superficial samples (Fig. 2), decreasing with the depth (Fig. 3). In this area no TCB was detected. The gamma HCH contents are below the detection limit (0.1 ppm).

The existence of secondary focuses outside of AF, detected by aerial photos of 1989 (areas with geometric patterns and white colour and texture) was confirmed in point CM 01. Here HCH and other substance were identified. This point can be considered a "hot spot", with 8300 ppm of total HCH (Fig. 2).

The suspicion that neighbourhood population was using HCH to fill holes in the access road, in embankments and in the constructions of the residences was confirmed in the samples CME 01 and 03 with contents of 0.1 and 14 ppm total HCH, respectively (Fig. 1).

It is presumed that contaminated dust blown from the industrial area represents one of the main contamination risk, affecting the population in nearby houses, cattle, pastures and small plantations. Air borne HCH is being investigated in the neighbourhood of AF. The groundwater path is of secondary priority, since wells are no longer in use.

5 DISCUSSION AND CONCLUSIONS

The following conclusions can be made:

- The attempt of "lime remediation", aiming to the dechlorification of HCH, did not eliminate the pollutants. A great part of the soil still exhibits high levels of contamination, with higher values than 4000 ppm total HCH.
- As by-product of this "remediation" process TCB was formed with concentrations between 140 and 2160 ppm in the superficial horizon. Its propagation to deeper levels, below 80 cm, cannot be proven.
- HCH migrated vertically to depths > 2 m, reaching and infiltrating the clay horizon. The probability of a HCH propagation to the groundwater and its horizontal displacement is high, facilitated by the existence of sand intercalations in the geological profile. The water table varies between 1.1 m and 1.80 m in AF.
- The quite erratic distribution of HCH and TCB in the surface horizon is probably due to the heterogeneous and incomplete mixture of the soil with lime. The application of lime resulted in reworking of the surface and consequently to a dissemination of the contamination in ACF.
- The most abundant isomers are alpha and beta HCH. The isomer gamma HCH (Lindane) is present in variable proportions, reaching maximum values of 420 ppm in CM 04.
- The high concentration of HCH in the soil, with about 30 tons of total HCH, the volume of polluted soil of around. 15.000 m^3 and its clay content turn difficult the decontamination by biological or physical-chemical methods (extraction) and extremely costly for thermal treatment (incineration).
- A workable solution is the construction of a controlled deposit for the contaminated material in the area (on site) with groundwater monitoring wells,

since the area is of high economical interest to real estate, aiming at its reuse for residential use.

- Probably not all of the secondary sources were found yet. More evidence could be obtained through interviews with the population. However it is believed that the secondary focuses are punctual and insignificant in terms of quantity.

In the case study, the technical objective of the joint effort of the working group is the future reuse of the presently abandoned site and its neighbourhood.

Since the initiation of the investigations in 1996 many more HCH deposits were identified by the working group, most of them in strong conflict with human health and land usage. The magnitude of the problem recently led to some reflections about environmental policies, the fate of the sites and the final destination of contaminated land. There are still lacking containment and remediation technologies for contaminated soils in Brazil. Moreover authorities do not yet consider the temporary containment of contaminated soil an environmentally acceptable and economically feasible solution to diminish or eliminate direct risks for the population but rather propagate total clean-up solutions which mostly are unreal.

Under these aspects the here presented activities as part of the German International Technical Co-operation shall show up new and up-to-date aspects for the establishment and implementation of standard methods for site investigation, risk assessment, site remediation and the definition of environmental policies geared to the problem of contamination by residues from the pesticide industry in Brazil.

MOVEMENT AND FATE OF MERCURY(0) IN THE SUBSURFACE OF A DERELICT CHLORALKALI PLANT AND IMPLICATIONS FOR REMEDIAL OPTIONS

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Key Words: mercury, site investigation, leachates, chemical speciation, distribution coefficient, mobility, contaminated plume

SUMMARY

Immediately downgradient from a derelict chloralkali plant mercury concentrations in the groundwater are exceeding maximum contaminant levels by factors of 50 to 100. Hence, the authorities requested that appropriate remedial measures be carried out. The site investigation showed that both the structure of the building and the subsurface (in places up to a depth of 12 m) are highly contaminated with mercury due to the past activities. The contamination plume in the groundwater has a length of more than 400 m. At this time, there is no immediate risk for any drinking water wells downgradient from the site.

KURZFASSUNG

Die Quecksilber-Konzentrationen im unmittelbaren Grundwasserabströmbereich einer ehemaligen Chloralkali-Fabrik überschreiten die zulässigen Gehalte um Faktoren von 50 bis 100. Die Behörden verlangten deshalb, dass entsprechende Sanierungsmassnahmen getroffen werden müssten. Die Detailuntersuchung hat nun gezeigt, dass sowohl die Bausubstanz des Gebäudes als auch der Untergrund (stellenweise bis auf 12 m Tiefe) aufgrund des langjährigen Betriebs stark mit Quecksilber belastet sind. Die Kontaminationsfahne im Grundwasser erstreckt sich über eine Länge von mehr als 400 m. Zur Zeit besteht für die unterliegenden Trinkwasserfassungen keine unmittelbare Gefahr.

RÉSUMÉ

Les concentrations de mercure dans les eaux souterraines en aval d'une ancienne usine de chlorures alcalins excèdent les limites légales d'un facteur 50 à 100. Les autorités concernées ont par conséquent exigé la mise en oeuvre de mesures adéquates. Les études conduites sur le site ont mis en évidence une forte contamination au mercure aussi bien des constructions que du sous-sol (partiellement jusqu'à une profondeur de 12 m). Le front de propagation dans les eaux souterraines a dépassé les 400 m mais ne présente jusqu'à présent aucun danger pour des puits d'eau potable.

Contaminated Soil '98, Thomas Telford, London, 1998, 173–179

1. Introduction

Immediately downgradient from a derelict chloralkali plant mercury concentrations in the groundwater are exceeding maximum contaminant levels by factors of 50 to 100. Hence, the authorities requested that appropriate remedial measures be carried out. This paper reports on the site investigation, movement and fate of mercury in the subsurface of the plant and implications for remedial options. The evaluation of measures and the actual remediation will be described in a later paper.

2. Site History

The chloralkali plant was built in 1900. In the beginning the diaphragm process was used. In 1925 this process was replaced by the amalgam procedure. In it, the sodium cation was reduced to metallic sodium at the mercury cathode subsequently forming sodium amalgam. This amalagam was then treated with water yielding sodium hydroxide. The building housing the electrolytic cells was called "cell hall". Adjacent to this hall were two buildings containing huge tanks for the sodium chloride solution. The cell hall was enlarged in 1960 housing 46 cells containing either 500 kg (old cells) or 320 kg (new cells) of mercury. The cells were placed on high steel props and underlain by a wood floor. When replacing the spent graphite electrodes, metallic mercury was inadvertently spilled. Since the wood floor was rinsed once a week the liquid mercury was washed down to the floor of the hall (covered by a 20 cm thick concrete slab) through the spacing between the planks. From here it was rinsed into two parallel wastewater canals. Water and mercury droplets were then channeled into pits, pumped into vessels and treated with sulfide. In 1987 the plant was closed down.

3. Geology and Hydrogeology of the Site

The plant is located in an alluvial valley. During the last glaciation this valley was filled up with alluvial deposits consisting mainly of gravel and sands. After the end of this period terraces were formed by river erosion. The chloralkali plant is situated on the lowest terrace on the right bank of the river. In this area the bedrock (upper fresh water molasse) is about 18 m below ground level. The gravel layer is topped by 50 cm of fine-grained flood deposits. The groundwater table is on average 3.8 m below ground level (see Figure 1). Groundwater flows approximately parallel to the length axis of the plant underpassing the river bed. The hydraulic conductivity of the aquifer is between $5 \cdot 10^{-3}$ and 10^{-2} m/s, i.e., the alluvial deposits are highly pervious. Average groundwater flow velocity is about 33 m/d the maximum being 100 m/d. The closest drinking water well is approx. 2 km downgradient from the plant.

4. Sampling Programme

Structure of the Cell Hall Complex. The structure of the cell hall complex was divided into separate units (see Figure 2). Each structural element (floor, northern wall, western wall, southern wall, eastern wall, roof, etc.) of a unit was sampled (about one sample per 10 m^3). A total of 256 discrete samples were taken as cores or surface samples. 55 composite and 21 discrete samples were eventually analyzed for total mercury content.

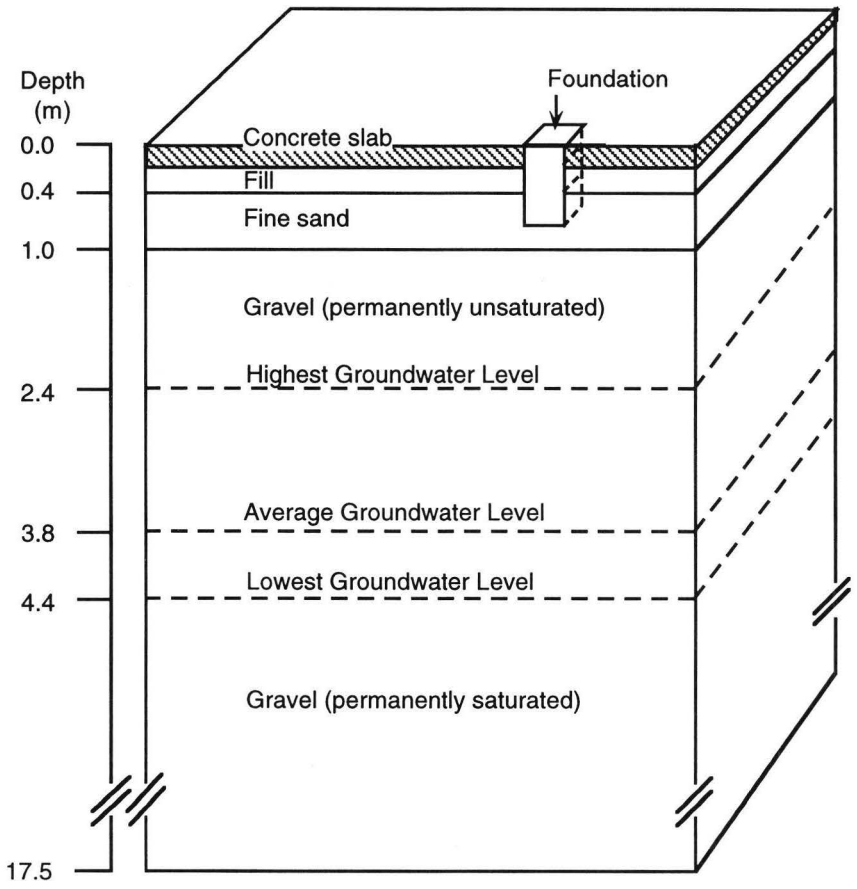

Figure 1: Stratigraphy below the Cell Hall Complex

Subsurface of the Cell Hall Complex. Borings were placed inside canals or pits where mercury containing water resided. A total of 29 borings were driven into the subsurface within the cell hall complex. Each of the 245 soil cores of 0.5 m to 1 m length was used as a discrete sample. In addition to the borings five shallow ditches were excavated within the former cell hall, outside of canals or pits. Samples were taken from the walls of these ditches at various depths.

5. Sample Preparation and Analytical Methods

The entire mass of a discrete sample was first crushed to a grain size of less than 10 mm. Composite samples were prepared mixing portions of the crushed samples. Subsequently, for the chemical analyses about 1 kg of each composite or discrete sample was crushed to a grain size of less than 2 mm.

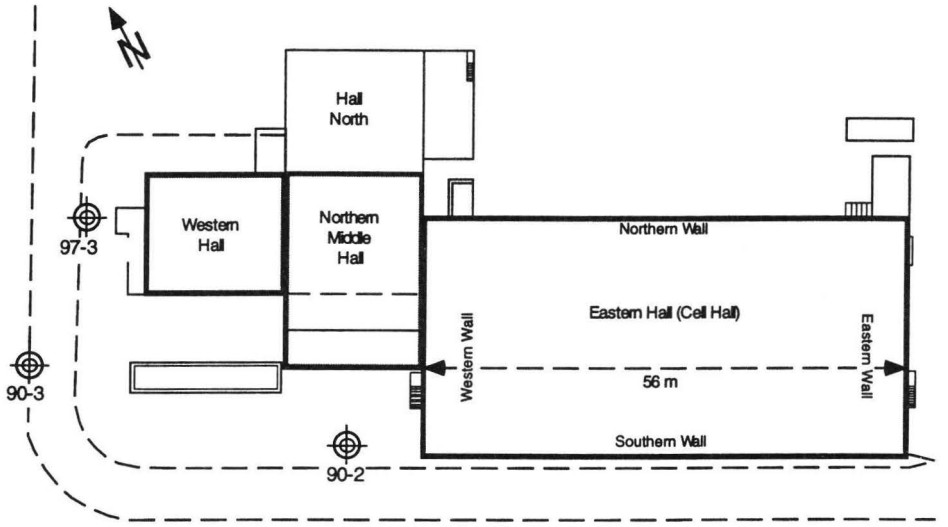

Figure 2: Overview Cell Hall Complex

Total Mercurcy (Hg_{tot}). About two grams of the solid sample were microwaved in a mixture of concentrated nitric acid and hydrogen peroxide (35 %). The suspension was filtered and subsequently diluted with nitric acid (10 %). The mercury concentration of the extract was determined with atomic absorption spectroscopy (AAS).

Elemental Mercury (Hg(0)). About one gram of the solid sample was extracted with an alkaline solution of cysteine (mercury(II) forms soluble complexes with cysteine while Hg(0) remains in the solid). After centrifuging the suspension, the extract was treated with a solution of bromine and potassium bromide in diluted nitric acid. Excess bromine was then reduced to bromide by adding sodium nitrite solution. The mercury concentration of the solution was determined as described above. The Hg(0)-content of the sample was calculated by subtracting the Hg(II)- from the Hg_{tot}-content.

Leaching Test. Carbon dioxide was bubbled through a suspension of about 50 g of the solid sample and 500 mL deionized water for 24 hours. 50 mL of the solution was then membrane-filtered (0.45 µm). The mercury concentration of the solution was determined as described above.

6. Results and Discussion

Structure of the Cell Hall Complex. All samples from the structure of the cell hall complex proved to be contaminated with mercury. The highest content (4'770 mg per kilogram dryweight) was found in a brick sample, the lowest in the roof tiles of the western hall (0.74 mg/kg dw). The results are summarized below:

1) the mercury contents of the structure of the western and northern middle hall, respectively, are much lower than those of the structure of the cell hall where the mercury vapors originated
2) the mercury concentrations in porous materials like wood and brick are higher than those of less porous materials like concrete

3) the total mass of mercury in the structure of the cell hall complex amounts to approximately 1300 kg

Mercury concentrations in the leachates of 11 samples of the cell hall complex ranged from 0.002 to 54 mg/L. The latter value corresponds to the maximum solubility of mercury under the conditions of the leaching test (CO_2-saturation, pH 6.2). Figure 3 shows that there is a linear correlation between Hg_{tot}-content in the solid and the leachate. Hg_{tot}-contents in leachates of samples which were not subjected to the leaching test were estimated using the function of the correlation curve. Given the Hg_{tot} content in both the solid samples and the corresponding leachates, the building material of the cell hall complex can be categorized with respect to contamination for the purpose of decommissioning and disposal.

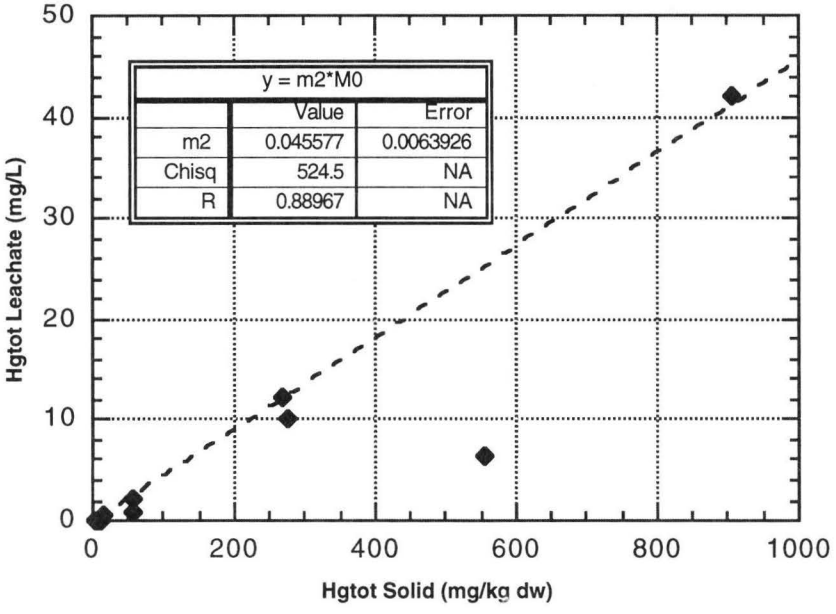

Figure 3: Hg_{tot}-content in Solid Samples versus Hg_{tot}-content in the Corresponding Leachates

Subsurface of the Cell Hall. Almost all soil samples proved to be contaminated with mercury. The highest concentration determined was 925 mg/kg dw. Some samples collected from the subsurface below pits even contained small mercury droplets. None of these samples were analyzed. The results are summarized below:

1) canals and especially pits are hot spots where the contamination reaches a depth of up to 12 m below ground (see Figure 4)
2) approx. 50 % of the mercury in the subsurface is still Hg(0)
3) mercury, in the form of either Hg(0) or Hg(II), was transported by groundwater from the hot spots into areas which had never been directly affected by infiltrating wastewater
4) the total mass of mercury in the upper 8 m of the subsurface below the cell hall complex is about 190 kg.

5) presently, the mercury flow (by diffusion of gaseous Hg(0)) from the vadose zone into the saturated zone of the subsurface is negligible

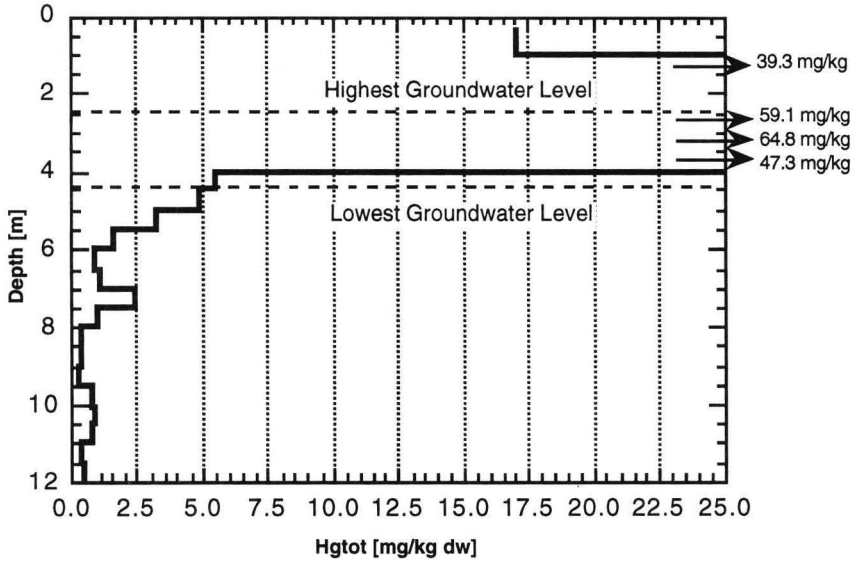

Figure 4: Mercury Concentration Profile next to a Pit

Subsurface downgradient from the Site. In order to assess the extent of the contaminated plume in the groundwater, several borings were drilled downgradient from the chloralkali plant. The results are summarized below:

1) mercury has been transported by groundwater over a distance of more than 400 m (concentration in groundwater samples at this distance: 1 to 2 µg/L; soil core samples: 0.1 to 1.5 mg/kg dw)
2) the thickness of the contaminated layer in the saturated zone is about 8 m
3) the average in-situ distribution coefficient (Kd_{is}) of mercury(II) is 500 L/kg
4) the total mass of mercury in the saturated zone downgradient from the chloralkali plant is in the range of 540 kg

The results of the site investigation are illustrated in Figure 5. 1300 kg mercury (65 % of the total mass) are contained within the structure of the cell hall complex while 540 kg (25 %) were distributed in the saturated zone of the subsurface downgradient from the cell hall complex forming a large contaminated plume. About 190 kg of mercury are in the upper eight meters of the subsurface below the cell hall complex.

7. Implications for Remedial Options

As indicated in Figure 5 even the removal of all mercury from the subsurface of the cell hall complex will have no effect on groundwater quality downgradient from the site on the short or medium term. Considering the high permeability of the aquifer, it is quite clear that any action to extract and remove significant amounts of mercury from the saturated zone would take decades which is simply not affordable. Drinking water wells

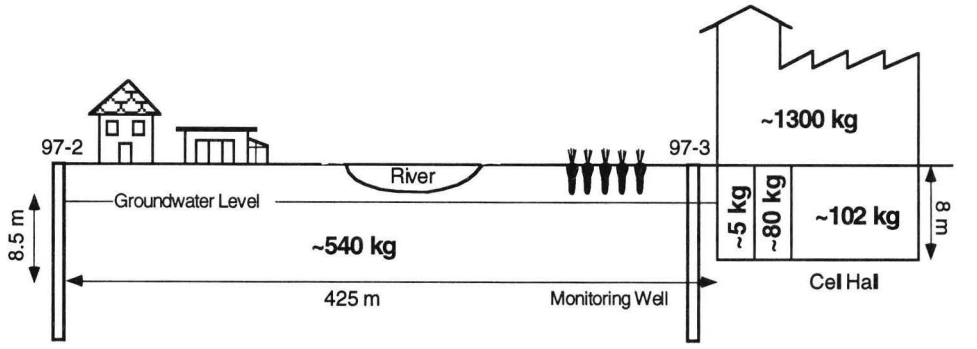

Figure 5: Schematic Overview of the Cell Hall Complex and Surroundings

are presently not expected to be affected by mercury. Most likely, there is no other option as to accept the natural attenuation by dispersion and distribution of mercury throughout the aquifer.

8. Conclusions

Hg(0) can be transported by water to great depths despite its low solubility (60 µg/L at 25 °C in the absence of oxygen and ligands[1]). Obviously Hg(0) was transported as very little droplets immersed in water. In the saturated zone of the subsurface Hg(0) is slowly oxidized to mercury(II) by the oxygen dissolved in groundwater. The dissolution rate is so low that Hg(0) was moved by the groundwater over a distance of a few dozens of meters before it is completely oxidized. Under the prevailing conditions in the groundwater (pH 7.8, chloride concentration: 10 mg/L), mercury(II) exists mainly as $Hg(OH)_2$. At this time, there is no immediate risk for the drinking water well 2 km downgradient from the site.

9. References

[1] Richter-Politz, I.; Geilhufe, C.; Sela, J. *TerraTech* **1995**, *2*, 26.

CHARACTERISATION OF NATURAL ATTENUATION IN AN INDUSTRIAL SITE CONTAMINATED WITH PHENOLS AND ALKYLBENZENES

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Key words: aromatic hydrocarbons, phenols, in-situ bioremediation, natural attenuation

SUMMARY

In the absence of environmental risk natural attenuation may represent an alternative for the long term management of groundwater plumes. This paper reports the preliminary results of the quantification of natural attenuation processes in a complex plume containing a variety of phenolic and alkyl benzene compounds. Natural attenuation rates for each of the compounds are calculated and discussed. The paper concludes with a discussion on the practical aspects of determining natural attenuation and the implications of this study in developing a management strategy based on natural attenuation.

Contaminated Soil '98, Thomas Telford, London, 1998, 181–190

INTRODUCTION

In the absence of environmental risk natural attenuation may represent a cost-effective alternative for the long term management of groundwater plumes. Natural attenuation is a groundwater management strategy which requires the identification and quantification of naturally occurring attenuation mechanisms (Weidemeier, et.al., 1996a). In appropriate circumstances the operation of natural attenuation may be sufficient to control the migration and eventually remediate a groundwater plume. Natural attenuation is increasingly popular as a remedial technique and there are many well documented examples of its application in the petroleum hydrocarbon and chlorinated solvents industries (Rifai, 1995 and USEPA, 1997).

In this study a preliminary assessment has been made of the role of natural attenuation in controlling the migration of a number of alkyl benzene and phenolic compounds. The study was undertaken in the context of an investigation aimed at assessing the risk and remedial alternatives for an industrial facility.

Natural attenuation is assessed on the basis of the existence of independent lines of evidence that demonstrate that natural attenuation is occurring (Weidemeier, et.al., 1996a). These lines of evidence can include:

- An observed reduction in contaminant mass or concentration with time.
- Geochemical evidence that biodegradation is on going
- Microcosm studies that isolate the biodegradation mechanisms

A body of monitoring data is needed for the first approach and while this may be present for some sites where remediation has been on-going, it will not be present in newly investigated or discovered instances of contamination. In these circumstances reliance is placed upon the latter two types of evidence and predictive modelling until sufficient evidence has been gathered. This study reports the initial assessment of natural attenuation using a combination of evidence related to contaminant concentrations, geochemical monitoring data and predictive modelling.

SITE DESCRIPTION

The site is an industrial facility which has utilised and stored a number of hazardous chemicals over a period of over 20 years. In part of the site a number of above ground storage tanks are used for the storage of a mixture of phenolic and alkylbenzene compounds. The area is approximately 20m by 60m in length and is currently surrounded by a concrete bund. Until 4 years ago the area was unbunded and any spillages would have impacted directly onto the underlying soil. With the construction of the bund and improved management practices the source of contamination has effectively been removed.

A site specific screening risk assessment conducted early in the investigation indicated that as a result of the on-going industrial end use the key exposure pathway was likely to be the off-site migration and ingestion of groundwater. A review of records indicated that there are no licensed groundwater abstraction wells within 3km radius downgradient of the site and beyond that the most likely eventual receptor was

considered a watercourse some 5 km distant. At the present time it is considered that there is no operational source-pathway-target relationship and the site represents a very low risk to the environment. Natural attenuation of the groundwater plume together with an in-situ treatment directed at the source remaining in the unsaturated zone was therefore given consideration as a remedial alternative that could meet the objectives of the long term restoration of the site.

METHODOLOGY

A series of boreholes and ground water monitoring wells were installed around the source area, up gradient of the presumed regional flow and in a series of locations downgradient of the source area (Figure 1). The purpose of the upgradient borehole was to obtain information on the natural water chemistry, while the downgradient wells were located to evaluate the behaviour of the contaminants as they migrated from the source zone. The maximum distance of the down gradient well from the source was 75m and this was dictated by the site boundary.

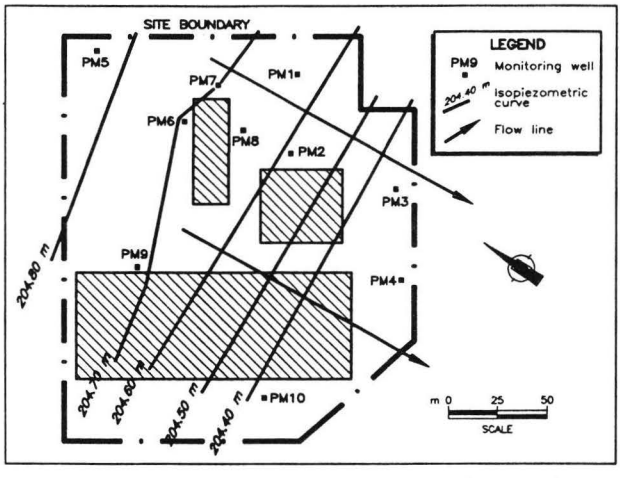

Figure 1 Site layout, borehole locations and piezometric map

Boreholes were advanced using continuous coring and all operations were performed in accordance with clean drilling protocols. In three locations inclined boreholes were used to obtain information about soil and ground water conditions directly under the tank farm. Piezometers were installed in all boreholes to enable the measurement of groundwater elevations and chemistry. The piezometers were 2½ inch diameter and constructed from PVC; screen settings (6 m in length) were located with about 2 m above the static water level encountered during drilling.

Samples of soil were collected and stored under refrigeration until dispatch to an accredited analytical laboratory. Samples were analysed for a variety of phenolic and alkylbenzene substances that were designated target compounds as a results of a review of compounds previously stored in the tanks.

Following well development and a period for stabilisation groundwater elevations in each monitoring well were measured and the wells were purged and sampled for the

range of target compounds and geochemical parameters. The latter included, temperature, conductivity, pH, dissolved oxygen, iron (II), nitrate, sulphate and alkalinity.

Sampling was undertaken using Grundfos MP-1 sampler operating at low flow rates to minimise in-well aeration and drawdown (the results of the independently undertaken pump test indicated that drawdown was minimal even at very high pump rates). The pump was connected to pre-cleaned PVC tubing and the outlet was connected to a flow through cell in which field probes were placed. All probes were pre-calibrated, and readings were measured upon stabilisation of the main parameters. The pump was decontaminated by rinsing and flushing with potable water between boreholes, and the tubing was completely changed after every borehole.

A round of sampling was undertaken in Spring 1996, groundwater elevations and gradient were measured approximately bi-monthly and at the end of the year a further round of groundwater monitoring was undertaken.

Predictive modelling was undertaken using an analytical model developed by Golder Associates, based on the equation described by Domenico (1987). The model simulates contaminant transport and degradation through an uniform, homogeneous and isotropic unconfined aquifer, assuming steady state one-dimensional groundwater flow and three-dimensional dispersion/diffusion phenomena.

RESULTS

GEOLOGY AND HYDROGEOLOGY

The site is underlain by fluvioglacial quaternary sediments, composed of silty gravel with sands alternated with finer silty sediments. The aquifer is unconfined and groundwater was encountered at an average depth of 4-5 m below ground level. Groundwater elevation data plotted in Figure 1 confirm the direction of the flow to the south as predicted from regional maps, with a hydraulic gradient of about 3‰. An average hydraulic conductivity of 2.00E-4 ms^{-1} was calculated from a long term pumping test and a porosity of 0.25 was estimated based on the stratigraphic conditions. The effective groundwater velocity was predicted via probabilistic approach and 50th percentile (equal to 74 m yr^{-1}) and 95th percentile (equal to 90 m yr^{-1}) were calculated. These figures were subsequently used for the modelling to act as a reasonable most probable and worst case for the conditions encountered.

The results of the bi monthly monitoring presented in Figure 2 illustrate a marked seasonal variation in the water level of approximately 1.5 m, with extremes of more than 2.8 m. The water flow direction does however remain constant during this fluctuation.

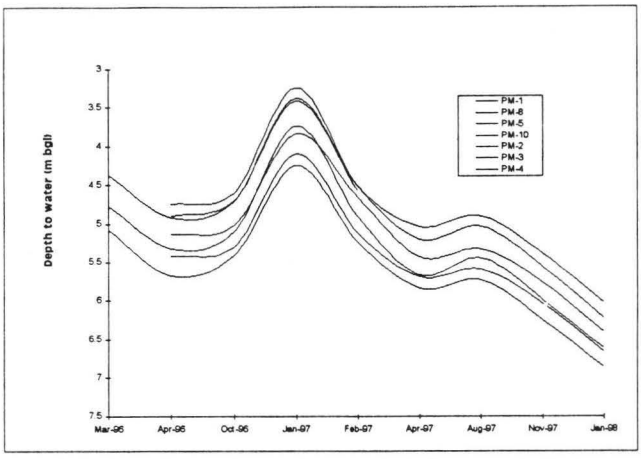

Figure 2 Results of bi-monthly groundwater monitoring

CHEMICAL ANALYSES

The results of total phenol and total alkylbenzene concentrations are summarised in Table 1 for the two monitoring occasions. Grouping the data hides differences in the behaviour of individual compounds but does give an indication of overall contaminant behaviour.

In the first set of data (April 1996) rapid decreases in contaminant concentration are evident along the direction of groundwater flow for each class of compounds analysed. A particularly high initial concentration of one compound, namely, 4-methyl phenol (400 mg l^{-1}) was reported near the source area. It may be seen that contamination rapidly attenuates from the source zone to the site boundary.

During the second monitoring round (March 1997) reductions in the concentration of contamination at the source are apparent with respect to phenols (as a result of reduction in 4-methyl phenol) while the concentration of alkylbenzenes is constant. Within the downgradient plume the rate and magnitude of apparent alkylbenzene attenuation is quite different from that measured a year earlier. Concentrations at the site boundary increasing from 0.43 to 3.73 mg l^{-1} largely due to an increase in concentrations of total xylenes.

Table 1 Summary of results for chemical analyses

Location	Total Phenols - mgl^{-1}		Total Alkylbenzenes - mgl^{-1}	
	Apr-96	Mar-97	Apr-96	Mar-97
PM5 - upgradient	<0.001	0.023	0.002	0.019
PM6 - upgradient	0.11	-	0.106	-
PM8 - in source zone	575	40.5	33	27
PM2 - down gradient 25m	65	10.4	24	6.57
PM3 - down gradient 75m	0.169	0.986	0.43	3.73

For the purposes of initial evaluation natural attenuation rates for each compound were approximated assuming that the plume was in steady-state and that contaminant degradation followed first order kinetics. The natural attenuation rates calculated using this method are a product of all the processes operating in the plume and not solely due to biodegradation. The results are presented in Table 2.

Table 2 Results of calculation of natural attenuation rates

A) Results for sampling undertaken in April 1996

Compound	74 m year^{-1} *			90 m year^{-1} *		
	K	$T_{1/2\ (days)}$	r^2	K	$T_{1/2\ (days)}$	r^2
phenol	0.0122	57	0.99	0.0148	47	0.99
2 - methylphenol	0.0125	55	0.99	0.0152	46	0.99
4 - methylphenol	0.0122	57	0.99	0.0148	47	0.99
2, 4 - dimethyl phenol	0.0075	93	1	0.0091	76	1
toluene	0.0043	161	1	0.0052	133	1
ethylbenzene	0.0075	92	0.96	0.0091	76	0.96
styrene	0.0096	72	0.98	0.0117	59	0.98
m & p xylene	0.0090	77	0.96	0.0110	63	0.96
o xylene	0.0052	133	0.98	0.0063	109	0.98
1 ethyl, 2 methylbenzene	0.0030	231	0.89	0.0037	188	0.89
1, 2, 4 trimethylbenzene	0.0039	178	0.91	0.0048	145	0.91

B) Results for sampling undertaken in March 1997

	74 m year^{-1} *			90 m year^{-1} *		
	K	$T_{1/2\ (days)}$	r^2	K	$T_{1/2\ (days)}$	r^2
phenol	0.0087	80	0.99	0.0106	65	0.99
2 - methylphenol	0.0054	129	1	0.0065	106	1
4 - methylphenol	0.0048	143	1	0.0059	118	1
2, 4 - dimethyl phenol	0.0041	169	1	0.0036	191	1
toluene	*0.0015*	*473*	*0.25*	*0.0018*	*389*	*0.25*
ethylbenzene	*0.0024*	*288*	*0.73*	*0.0029*	*237*	*0.73*
styrene	n.d.					
m & p xylene	0.0022	322	0.92	0.0026	264	0.92
o xylene	0.0032	217	0.98	0.0039	178	0.98
1 ethyl, 2 methylbenzene	*0.0003*	*2122*	*0.7*	*0.0004*	*1745*	*0.7*
1, 2, 4 trimethylbenzene	*0.0002*	*2932*	*0.65*	*0.0003*	*2411*	*0.65*

k = natural attenuation rate

$T_{1/2\ (days)}$ = half life in days

r^2 = correlation coefficient

* effective groundwater velocity

results in italics indicate that first order decay assumption is not observed

It may be seen that in April 1996 the first order model was representative ($r^2 > 0.8$) of the observed behaviour for all the individual parameters of interest. As expected half lives for individual contaminants vary. With phenols this appears to reflect increasing molecular weight and similar patterns have been observed in laboratory studies (Thomas and Lester, 1993). The pattern is repeated for alkyl benzenes though

toluene is an exception. This may reflect the very low starting concentration of this compound (0.22 mgl^{-1}). The half lives are within the range of natural attenuation rates reported in the literature, though 1,2,4 trimethylbenzene is sometimes considered more recalcitrant than other BTEX type compounds (Wiedemeier, et. al., 1996b).

During the second sampling event quite different patterns of contamination are evident. For phenols the first order behaviour holds, but half lives of contaminants have increased, more than doubling in some instances (2 and 4 methyl phenol). For alkylbenzenes the first order equation is only applicable to o, m & p xylene as a result of increased concentrations of other compounds in borehole PM2 with respect to the area around the source (PM8).

GEOCHEMICAL DATA

The groundwater was found to have an average temperature of 14°C, a pH of between 6.5, and a conductivity of between 430 - 800 us cm^{-1}. A summary of other key groundwater geochemical characteristics in relation to the location of the contaminant inputs is presented in Tables 3 and 4 and a transect through the site along the direction of groundwater flow is illustrated in Figure 3.

Table 3 Summary of results for geochemical indicators - April 1996

Location	O_2 mgl^{-1}	Fe (II) mgl^{-1}	NO_3 mgl^{-1}	SO_4 mgl^{-1}	Alkalinity mgl^{-1}
PM5 - upgradient	1.7	0	10	50	1.6
PM6 - upgradient	1.3	0	5	30	0.9
PM8 - in source zone	0.1	10	5	5	1.7
PM2 - down gradient 25m	0.1	30	10	0	2.6
PM3 - down gradient 75m	0	10	5	0	2.4

Table 4 Summary of results for geochemical indicators - March 1997

Location	O_2 mgl^{-1}	Fe (II) mgl^{-1}	NO_3 mgl^{-1}	SO_4 mgl^{-1}	Alkalinity mgl^{-1}
PM5 - upgradient	1.4	0	10	34	-
PM6 - upgradient	1.8	5	5	4	-
PM8 - in source zone	0.5	0	5	3	-
PM2 - down gradient 25m	0.7	5	10	31	-
PM3 - down gradient 75m	0	7	5	9	-

It may be seen that the upgradient water quality is characterised by a dissolved oxygen concentration of 1.7 mg l^{-1}, and sulphate concentration of 50 mg l^{-1}. On entering the source significant changes occur in the concentrations of key parameters as would be expected if biodegradation were occurring (Rifai, et al. 1995). Down gradient of the source both sulphate and oxygen remain in low concentrations while iron increases further to a maximum of 30 mg l^{-1}. At the site boundary iron remains elevated and oxygen and sulphate remain depleted, indicating that reducing conditions remain. Nitrate does not behave as expected and does not follow any particular trends, the reasons for this are not apparent. On the second occasion of monitoring

these patterns are not consistent with no apparent trends for sulphate, iron(II), or nitrate.

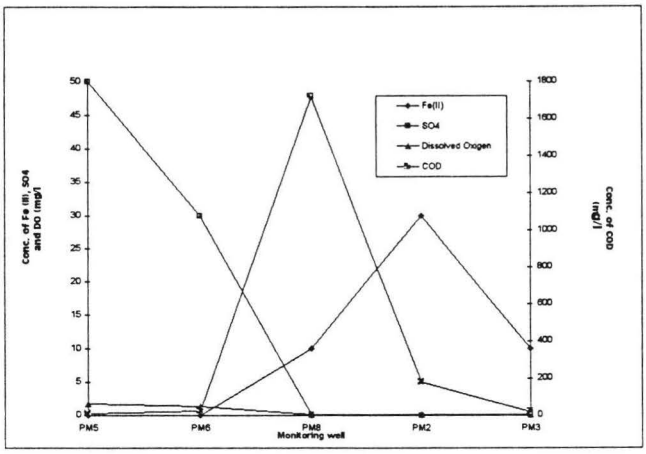

Figure 3 Transect along length of contaminant plume indicating key geochemical parameters

MODELLING RESULTS

The observed contaminant degradation patterns were used to predict the behaviour of key contaminants beyond the site boundary using the method described by Domenico (1987) calibrated using the observed concentrations. An example of simulation output for total xylenes is presented in Figure 4. Risk Based Health Criteria (RBHC) derived from literature were selected in order to define acceptable contaminant thresholds. In the example illustrated (Figure 4) concentrations of total xylenes decrease below the RBHC for the worst case assumption (i.e. groundwater flow velocity equal to 90 m yr^{-1}, half lives derived from March 1997) at about 200 m distance from the source, and thus reinforcing the absence of any potential risk to human health.

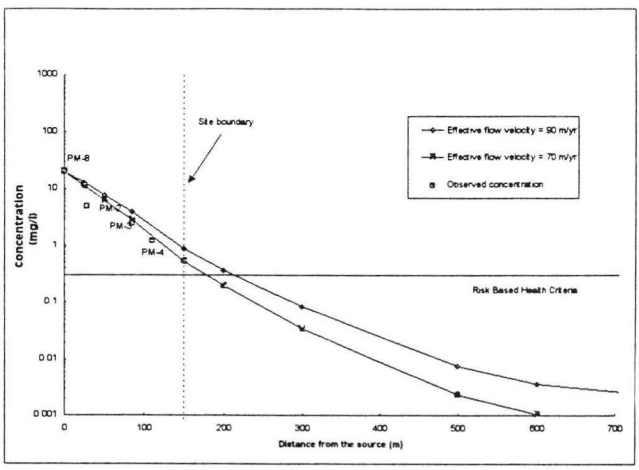

Figure 4 Result of modelling to predict the fate of contaminants

DISCUSSION

The results presented above represent an initial evaluation of on-going natural attenuation processes at an industrially contaminated site. The decision to proceed with this evaluation was made on the basis of the first round of sampling (April 1996) when reductions in contaminant concentration and geochemical changes in the groundwater plume were considered sufficient evidence that the plume is biologically active and that attenuation was on going. The degradation of this mixture of compounds was not un-expected as both groups of contaminants have been shown to be degradable under a variety of redox conditions. When coupled with the results of predictive modelling and the low risk status of the site natural attenuation was believed to represent a viable alternative for ground water, while contamination located in the unsaturated zone would be addressed by a separate technology.

In the second round of analysis, patterns of contamination have altered particularly with respect to the concentrations of alkylbenzenes in the plume. The geochemical patterns established in the first round of sampling are also no longer apparent and confidence in our earlier predictions was decreased. Nevertheless predictive modelling indicated that contaminants would be degraded to concentrations protective of human health within 500m of the site boundary. The observed concentrations may be the result of fluctuations in the water table causing release of additional contaminants and re-aeration of the plume along its length. Results that indicate apparent zones of oxic and anoxic within aquifers are not uncommon and can be the result of difficulties in measuring oxygen sensitive parameters (Swindoll and Troy, 1996). (It is interesting to note that without regular water level monitoring the 1m rise and fall in water levels that occurred in January 1997 would have been completely missed).

However there is insufficient evidence at present to fully understand these trends and a two year quarterly groundwater monitoring programme is proposed to fully validate these initial findings. Monitoring for methanogenesis will be incorporated to determine the contribution expected form this particular pathway. At the same time a remedial action directed towards source reduction in the unsaturated zone has been initiated.

CONCLUSION

This case study indicates the difficulties that can occur in establishing and validating the occurrence of natural attenuation in the absence of a body of groundwater monitoring data.

The characterisation of natural attenuation in a newly discovered site requires substantial effort and over a timescale that may not always be acceptable. In this case the quantification of natural attenuation was coupled with a remedial programme addressed at the source of the contamination in an integrated strategy.

Physical constraints on access can also affect the feasibility, in this study the future location of monitoring wells off site will be useful in confirming the results of the predictive modelling.

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NATURAL ATTENUATION: A BASIS FOR DEVELOPING EXTENSIVE REMEDIATION CONCEPTS

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Key words: chlorinated hydrocarbons, extensive remediation concepts, in situ bioremediation, natural attenuation, natural biodegradation, examination

SUMMARY

Based on an evaluation of more than 15 sites in the Netherlands contaminated with chlorinated hydrocarbons , a 'quick and dirty' scan for determining the potential of natural attenuation has been developed. For the investigated sites a comprehensive examination of the chemical and physical characteristics was made. Although natural biodegradation is affected by a complex combination of environmental factors, it was concluded that a first reliable estimation of the potential of natural attenuation can be obtained from only three simple parameters, e.i. the sulphate- and soluble organic carbon concentrations and the ratio between vinylchloride and di-chloroethene. Four situations can be distiguished rating the perspective of natural attenuation as remediation option from directly applicable to not applicable. Moreover, using the same scan, the posibilities for extensive stimulation of natural attenuation can be determined.

KURZFASSUNG

Tauw hat ein Verfahren zur Grobbestimmung des Potentials natürlicher Prozesse zum Abbau von Schadstoffen entwickelt. Grundlage bildeten mehr als 15 mit Chlorkohlenwasserstoffen kontaminierte Gelände in den Niederlanden. In einer Detailstudie wurden die chemischen und physikalischen Eigenheiten der Gelände ermittelt. Der natürliche Abbau von Schadstoffen wird von einer Reihe komplexer Umweltfaktoren beeinflußt. Dennoch hat sich gezeigt, daß die Ermittlung dreier Parameter, nämlich Sulfate, lösliche Organokohlenwasserstoffe sowie das Verhältnis zwischen Vinylchlorid und Dichlorethen, ausreichend ist für eine relativ zuverläßige Ersteinschätzung des vorhandenen Abbaupotentials. Es wurden vier Kontaminationssituationen unterschieden, in denen die Perspektiven einer Nutzbarmachung natürlicher Abbauprozesse zu Sanierungszwecken von "sehr gut" bis "nicht vorhanden" variieren. Das entwickelte Verfahren eignet sich ebenfalls zur Ermittlung von Möglichkeiten zur weitgehenden Stimulierung des natürlichen Abbaus von Schadstoffen.

RÉSUMÉ

Sur la base d'une évaluation de plus de 15 sites contaminés par des hydrocarbures chlorés aux Pays-Bas, il a été développé un scanner "rapide et grossier" pour déterminer les possibilités d'atténuation naturelle. Pour les sites qui ont été étudiés, un examen détaillé des caractéristiques chimiques et physiques a été effectué. Bien que l'atténuation naturelle ait été affectée par une combinaison complexe de facteurs de l'environnement, il a été possible d'obtenir une première estimation fiable des possibilités d'atténuation naturelle seulement à partir de trois simples analyses. Nos résultats montrent que sur la base des concentrations de sulfate et de carbone organique soluble combinées avec le rapport entre le chlorure de vinyle et le dichloréthylène, on peut distinguer quatre situations principales. Ces situations distinguent la perspective pour une atténuation naturelle comme un remède technique de directement applicable à non-applicable. Par ailleursé en utilisant le même scanner, on peut déterminer les possibilités d'une énorme stimulation de l'atténuation naturelle.

Contaminated Soil '98, Thomas Telford, London, 1998, 191–196

INTRODUCTION

Natural attenuation refers to all processes that help to reduce the concentrations and total mass of contaminants in the subsurface (e.g. biological and chemical degradation, irreversible sorption or precipitation and dispersion). Most of the natural attenuation processes have not yet been explicitly investigated in the soil remediation practice. Hence, the prospects of natural attenuation as a cost effective and environmentally beneficial soil remediation technique are neglected in practice.

In this paper we present a practical investigation strategy that can easily be applied to sites contaminated with chlorinated hydrocarbons, and especially chloroethenes. The strategy gives a first idea of the extent to which natural attenuation takes place, and of the limiting conditions for natural biodegradation. Once these conditions are known, extensive remediation concepts can easily be developed and be compared to more classical and more costly intensive remediation concepts.

The strategy is developed on the basis of the results of field investigations into natural attenuation at more than 15 contaminated sites in the Netherlands, combined with our experience with extensive in-situ remediation.

RESULTS OF FIELD INVESTIGATIONS

Analogous to Wiedemeier *et al.* (1996) the field investigations into natural biodegradation were mainly focused on:

1. the presence of degradation products of chloroethenes;
2. the characterisation of redox situation;
3. the availability of suitable substrate (electron donors) for reductive dechlorination.

At every site, groundwater measurements were carried out in the source and plume zone with an average of approximately 6 monitoring wells per site. The results of the field investigations show that for the Dutch situation four major situations can distinguished, which give an indication of the occurence of natural biodegration of chloroethenes at contaminated sites. These four situations are summarised in table 1.

Table 1: Different situations encountered in field investigations

Situation	ratio VC/DCE in plume	concentrations of sulphate and DOC in plume	conclusions
1	> 0.1	SO_4^{2-} < 5 mg/l DOC > 10 mg/l	Complete reductive dechlorination is likely
2	< 0.05	SO_4^{2-} < 5 mg/l DOC < 10 mg/l	Complete reductive dechlorination may be possible
3	< 0.05	SO_4^{2-} > 20 mg/l DOC < 10 mg/l	Complete reductive dechlorination is unlikely
4	< 0.05	SO_4^{2-} > 20 mg/l DOC > 10 mg/l	Complete reductive dechlorination is unlikely

In the following, these situations will be discussed in more detail.

Presence of degradation products
At all investigated sites the following original and degradation products of chloroethenes were measured in the source and plume zone: tetrahloroethene (PCE), trichloroethene (TCE), cis-dichloroethene (DCE), vinylchloride (VC), ethene and ethane. For each investigated monitoring well the ratio between original and the degradation products and the ratio between the individual degradation products were calculated.

At all investigated sited two situations in the plume zone could be distinguished:

1. $\frac{VC}{DCE} > 0.1$ and $\frac{ethene}{VC} > 0.1$
2. $\frac{VC}{DCE} < 0.05$ and $\frac{ethene}{VC} < 0.05$

It was striking that at none of the sites an 'in between' situation was encountered.

Redox characterisation
For the characterisation of the redox situation the concentrations of electron acceptors (or its reduced products) were measured upstream, in the source zone, the plume zone and if suitable monitoring wells were available downstream outside the contaminated area. The following electron acceptors or its reduced products were measured: O_2, NO_3^-, Fe^{2+} ,SO_4^{2-} and methane.

From the absolute concentrations in the source or plume zone and the relative concentrations of electron acceptors compared to the concentrations upstream (background level) the following redox conditions could be derived:

Table 2: redox conditions

concentrations (mg/l)	aerobic conditions	denitrifying conditions	iron reducing conditions	sulphate reducing conditions	methanogenic conditions
O_2	> 0.5	< 0.5	< 0.5	< 0.5	< 0.5
NO_3^-	= background level	= background level	< 1	< 1	< 1
Fe^{2+}	= background level	= background level	2x background level	2x background level	2x background level
SO_4^{2-}	>20[a)]	> 20[a)]	> 20[a)]	< 5	< 5
CH_4	= background level	= background level	= background level	= background level	2x background level

[a)] In The Netherlands sulphate concentrations in groundwater are in natural situations almost always larger than 20 mg/l.

Availability of substrate
For the reductive dechlorination of chlorinated solvents a suitable substrate (C-source and electron donor) must be available in the groundwater. This substrate can either be of natural origin (e.g. humic acids) or entered the into the soil as an anaerobically degradable co-contaminant. Because a lot of different organic compounds can be used directly or in a roundabout way as a substrate for the dechlorinating micro-organisms, it is impossible to find one specific method for determining the amount of suitable and available substrate in groundwater.

In order to find the best possible method for the amount of suitable and available substrate, three different parameters were tested: DOC (Dissolved Organic Carbon), COD (Chemical Oxygen Demand) and BOD (Biological Oxygen Demand). From these, the DOC values rendered the most consistent results.

In all situations in which it was concluded that natural biodegradation of chlorinated solvents occurs, DOC levels were higher than 10 mg/l. However, in some cases DOC levels over 10 mg/l were encountered while it was concluded from chloroethene concentrations that biodegradation did not occur significantly. In these cases the DOC present presumable cannot serve as a substrate for dechlorination.

Overall

From the results of the site investigations it was concluded that in practice reductive dechlorination of chloroethenes takes place in two steps, by two different populations of micro-organisms. The first step is dechlorination from PCE and TCE to DCE, which seems to take place in almost every anearobic aquifer. The second step is the dechlorination from DCE to VC and ethene. For this step redox conditions are more critical, and therefore determining for the potential of natural attenuation as a remediation technique.

At most sites we observed a clear relation between the extent in which dechlorination takes place, sulphate concentrations and DOC-concentrations. From the relation between sulfate concentrations and the conversion of DCE to VC and ethene, it can be concluded that for this conversion step at least sulfate reducing conditions are essential (see table 1).

The relation between dechlorination and DOC-concentrations can be explained assuming a different substrate affinity for the two dechlorinating populations. Under substrate limiting conditions the first step may be favourable. This effect can be enhanced by substrate competition between sulphate reducing bacteria and dechlorinating bacteria.

Indications that mainly two different populations of micro-organisms are responsible for the complete reductive dechlorination of PCE to ethene in soil are also found in other studies (Gerritse *et al.* (1998), Gerritse *et al.* (1997), Tonnaer *et al.* (1997)).

INVESTIGATION STRATEGY

In the Dutch situation, the extent to which natural attenuation takes place seems to be mainly controlled by two parameters, i.e. sulphate-concentration and substrate availability (expressed as DOC). Since the conversion from DCE to VC seems to be the most critical step, we use the VC/DCE ration to express the extent of natural attenuation. In other words, by measuring the sulphate- and, DOC-concentrations combined with the VC/DCE ratio measured, a quick scan of the potential of natural attenuation as remediation technique at a site can be made.

In order to determine whether natural attenuation can function as a remediation technique, or biodegradation needs to be stimulated, the following investigation strategy can be followed:

1. measure sulphate, DOC, DCE and VC in the plume zone
2. compare the results with table 1.
3. select the remediation concept from table 3

Table 3: Selection of remediation concepts

Situation (see table 1)	conclusion	concepts	action
1	You can have faith in natural attenuation	remediation by natural attenuation	limited monitoring of degradation products in monitoring wells
2	Natural attenuation proceeds slowly due to substrate deficiency	remediation by natural attenuation or extensive stimulation of biodegradation	intensive monitoring of DOC and degradation products addition of suitable substrate
3	Natural attenuation will not proceed sufficiently due to substrate deficiency enhanced by substrate competition	extensive stimulation of biodegradation	additional study on optimal concept for stimulation biodegradation
4	Natural attenuation will not proceed sufficiently due to lack of suitable substrate or other inhibiting conditions.	extensive stimulation of biodegradation may be possible	elaborate study on limiting conditions for biodegradation is essential

DISCUSSION AND CONCLUSIONS

The presented investigation strategy is a very efficient method for assessing the potential of natural attenuation as a remediation option for soil contaminated with chloroethenes. Although the method is still in development and adjustments will be made, we believe in the practical applicability in the Dutch situation. The applicability for contaminated sites outside the Netherlands needs to be investigated.

In most situations the quick scan will give sufficient information on how to proceed with natural attenuation. Of course more elaborate field investigations render extra information that can be valuable when remediation concepts are worked out in more detail.

At the moment, guidelines for the application of natural attenuation as a remediation technique are in development under the Dutch research programme on biological In-Situ remediation (NOBIS). In the development of these guidelines attention is paid to elaborate investigation strategies as well as to quick scans such as presented in this article.

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INTRINSIC DECHLORINATION OF 1,2-DICHLOROETHANE AT AN INDUSTRIAL SITE

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ABSTRACT: Bioremediation strategies for an industrial site located in the Rotterdam Harbor Area, the Netherlands and contaminated with 1,2-dichloroethane (1,2-DCA), are under investigation. The contamination is present in a confined anaerobic aquifer. The objective of the research is to assess the potential of intrinsic (bio)degradation and enhanced biodegradation as effective risk reducing measures. Close to the contaminant source, 1,2-DCA is present at concentrations up to 500 mg per liter. From the possible intrinsic dechlorination products of 1,2-DCA (i.e. 2-chloroethanol, vinylchloride, chloroethane and ethene), vinylchloride (VC) is occuring at relatively high concentrations (up to 2 mg/liter). The type, rate and parameter dependency of the dechlorination processes occurring in this aquifer are currently being investigated by analyzing groundwater concentration profiles of the dechlorination products and by performing laboratory studies with material from the contaminated site. First results indicate that natural attenuation alone, is not sufficient to prevent the plume from further spreading. Therefore a field study at pilot-scale is underway to evaluate remediation strategies which are designed from screening studies at the laboratory scale.

INTRODUCTION

The current research takes place at a vinylchloride (VC) production facility located at the Rotterdam-Botlek area, The Netherlands. Due to accidents, the groundwater at the location is contaminated with 1,2-dichloro-ethane (1,2-DCA). The contamination is currently being contained with a pump & treat technology. The current study was initiated to investigate the potential for natural attenuation, possibly in combination with a biologically activated zone (BAZ), to reduce the risk of pollutant spreading

Transformation pathways of 1,2-DCA. 1,2-DCA is degradable under both oxic and anoxic conditions. Aerobically it is oxidized to 2-chloro-ethanol and 2-chloro-acetate which is then dehalogenated oxidatively and further mineralized (Janssen et al. 1984, Van den Wijngaarden et al. 1992). A first review of the relevant literature did not reveal any information on the transformation of 1,2-DCA under mildly reducing conditions (denitrification, iron reduction). Under sulfate reducing and methanogenic conditions, 1,2-DCA can be reductively dehalogenated via vinyl-chloride (VC) and

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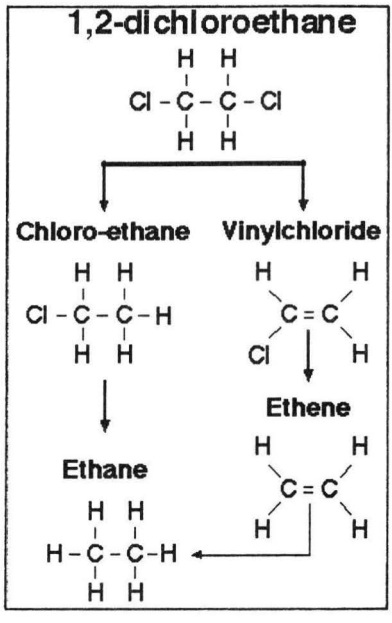

FIGURE 1. Transformation pathways of 1,2-DCA under sulfate reducing and methanogenic conditions.

chloroethane (CA) to yield ethene and ethane (Figure 1). The formation of VC from 1,2-DCA probably results from abiotic hydrolysis (Jeffers et al, 1989) while the other steps are believed to be biotic (Belay and Daniels 1987, Egli et al, 1987).

Site description. The production facility is located in the Rotterdam Harbor Area, The Netherlands. Since the site is located in a sedimentation area, the aquifer material is highly heterogeneous (Figure 2). The geological situation is further complicated by the history of the site. A sand layer of about 4 m was applied to elevate the land and to make it ready for construction of buildings etc. In addition, sand pillars serving as foundation for the production facilities were constructed. At least two accidents have resulted in soil and groundwater contamination with 1,2-DCA in the past. Due to the presence of the sand pillars the DNAPL has quickly reached the groundwater as can be inferred from the relative high residuals which are still present within the sand pillars (Figure 2).

Objective. The objective of the present research is to investigate the potential of natural attenuation of 1,2-DCA at the site making use of intrinsic (bio)degradation processes and enhanced biodegradation to prevent spreading of the contaminant plume in the confined aquifer.

APPROACH

Field work was done to establish the prevalent redox conditions in the groundwater (Bjerg et al., 1995) and to assess the extension of the contamination. Special attention was paid to the presence of potential degradation products. First order estimates of degradation rates were made based on the assumptions (i) that degradation had taken place since the occurrence of the first 1,2-DCA spill about 10 years ago or (ii) that degradation takes place within the two years of travel time between the source of contamination and the wells which are in use for the current geo-hydrological isolation method (Bosma et al., 1997). For both approaches it was assumed that the dilution and dispersion would have affected the parent compound and the degradation products in the same way and that no loss of product (e.g. due to complete mineralization) has occurred in the course of

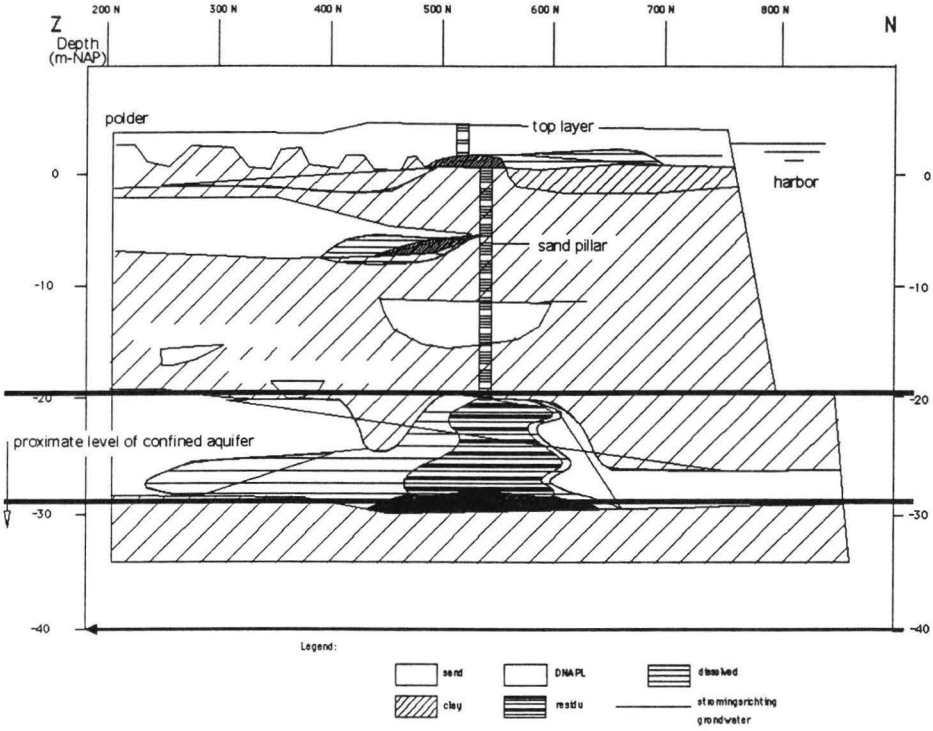

FIGURE 2. Cross-sectional view of the site (left: south; right north) and the vertical distribution of 1,2-DCA.

time. Thus, both the slow (10 year time of degradation) and the fast (2 year time of degradation) scenario's were believed to yield conservative estimates of the actual first order rate constants.

During the second phase of the project, the potential for intrinsic degradation was further investigated at the laboratory scale with material and groundwater from the site, amended with 1,2-DCA. Furthermore, several ways to enhance the intrinsic degradation rate, are evaluated in a pilot-scale field plot (Figure 3). The scenarios to be evaluated are inferred from laboratory scale screening tests.

RESULTS

The analysis of the macrochemistry revealed that the redox status of the groundwater is in the range from mildly to strongly reducing (i.e. from iron reducing to methanogenic). As organic constituents VC, ethene, and ethane were found, next to the parent compound 1,2-DCA (Table 1). Highest concentrations were in the high μM to mM range. The current geo-hydrological isolation procedure effectively contains the contamination within the boundaries of the site.

First order degradation rate constants were estimated following the procedure outlined in the APPROACH section (Table 1). The resulting

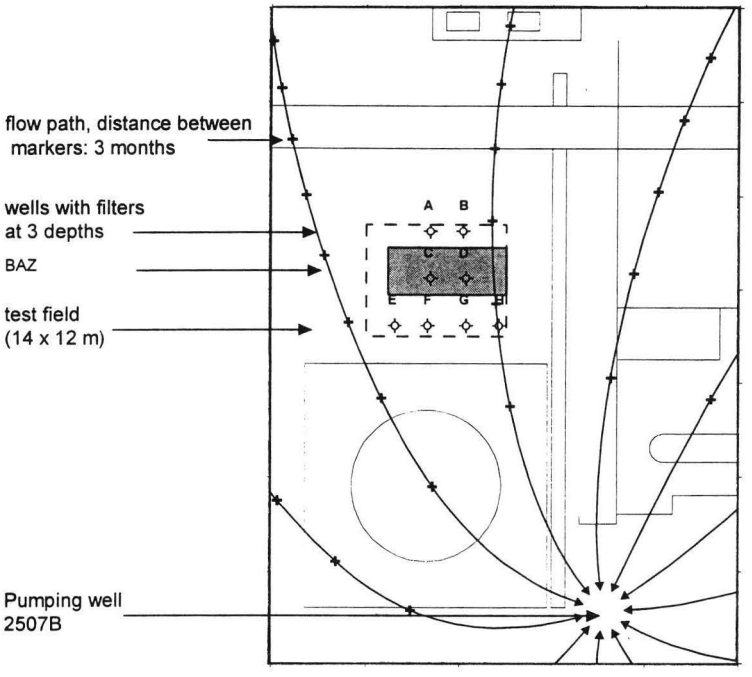

FIGURE 3. Plane view of the test field. The size of the location is about 10x15 m.

estimated half-lives of 1,2-DCA under field conditions vary from less than 1 year to over 30 years (Bosma et al. 1997).

Results of the laboratory tests for intrinsic biodegradation vary depending on the exact location where the aquifer material had been taken, illustrating the local heterogeneity with respect to biodegradation (Figure 4). Batch and column experiments with material withdrawn from the pumping wells P2507A, P2507B, and P2507C, gave an incomplete transformation of 1,2-DCA to ethene although 1,2-DCA was completely removed (Figure 4A). Ethene yields were 25±5%. Temperature experiments revealed a temperature optimum between 20°C and 30°C, indicative of biotransformation.

No spontaneous biodegradation of 1,2-DCA was found in samples obtained from the test field, which is located in the neighborhood of pumping well 2507B, although some traces of VC were found after more than for weeks of incubation, maybe due to a slow, abiotic degradation of 1,2-DCA (not shown). An immediate and stoichiometric transformation of 1,2-DCA to ethene was found after the addition of yeast extract (? mg/l) to the incubations, indicating the potential for a rapid degradation by reductive dechlorination through dihaloelimination (Figure 4B).

DISCUSSION AND OUTLOOK

The contaminated groundwater is mildly to strongly reducing. Evidence for a reductive transformation of 1,2-DCA to VC, ethene, and ethane

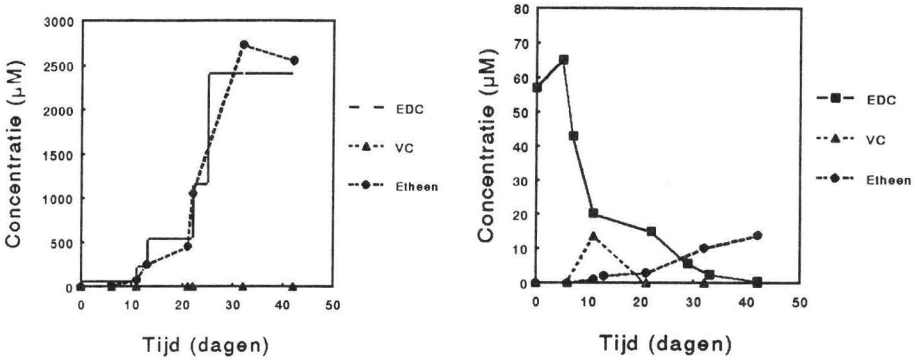

FIGURE 4. Spontaneous biotransformation of 1,2-DCA in samples from the pumping wells (A) and enhanced biotransformation in samples from the test field (B). No spontaneous biodegradation was observed in the samples from the test field (not shown).

is obtained from the field data. Conservative estimates of the half-life of 1,2-DCA at the site are in the range from 1 to 30 years.

Laboratory scale biodegradation appeared to be much faster with a half-live of 2 weeks or less. The nature of biodegradation appeared to depend on the origin of the samples. No spontaneous biodegradation was observed at the test field close to pumping well P2507B, while the material taken form the 3 pumping wells (P2507A-C) gave an immediate and complete biodegradation of 1,2-DCA although only 25±5% of the original 1,2-DCA was recovered as ethene. The absence of biodegradation at a portion of the site can very well explain the apparent slow rates of field-scale biodegradation as compared to laboratory scale biodegradation.

The perspective for the activation of biodegradation at the site is promising as based on the preliminary results with the addition of yeast extract. The field study will focus on a stimulation of the biodegradation of 1,2-DCA and VC, and on preventing the - undesired - accumulation of VC.

ACKNOWLEDGEMENT

This work is financially supported by the Netherlands Research Program for Biotechnological In-Situ Remediation (NOBIS), by the owner of the site, and by all participants.

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NATURAL ATTENUATION OF 60 PETROLEUM PLUMES AT PEASE AIR FORCE BASE, NEW HAMPSHIRE, USA

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Key Words: In situ groundwater remediation, natural attenuation, petrol hydrocarbons, BTEX

SUMMARY

A detailed study was performed at Pease Air Force Base, New Hampshire to document the natural attenuation of 60 petroleum plumes along the flightline refueling system. The study included the evaluation of electron acceptor and contaminant concentrations at each plume. To provide estimates of cleanup times, a simplified model was developed that could be used at each plume. This model takes into account groundwater seepage velocities, electron acceptor and contaminant concentrations, and decay rates. The results from this study indicated that natural attenuation is occurring at each of the plumes, that no single degradation process dominates, and that over 50 percent of the plumes will be remediated within 5 years.

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1. INTRODUCTION

At Pease Air Force Base (AFB), located in New Hampshire USA, military aircraft fueling and defueling operations were performed along a 3,450 meter flightline using a refueling system. The Flighline Refueling System was constructed in the 1950's and consisted of 10 pumphouses, 102 fueling/defueling hydrants, and 66 underground storage tanks. Between 1994 and 1996, the Refueling System was dismantled with 197 source areas either removed, cleaned and abandoned. Subsequent site investigates were performed that identified 60 separate dissolved petroleum hydrocarbon plumes that exceeded regulatory groundwater cleanup standards (Figure 1). During the Fall of 1996, groundwater samples were collected from each of the plumes. Results suggested that considerable benzene, toluene, ethylbenzene, xylenes, and naphthalene (BTEXN) contamination (up to 32.5 mg/L) still exists at many plumes. However, 11 of the 60 plumes identified during the site investigations, no longer had any regulatory exceedences. This suggested that natural attenuation was reducing BTEXN levels in these plumes.

This paper summarizes the results from the natural attenuation study and presents the results of a modeling tool used to evaluate the natural attenuation process as a remedial technology on a plume by plume basis.

2. BACKGROUND

Natural attenuation (NA) is a scientifically supported remedial action for hydrocarbon-contaminated media that has been successfully documented at numerous sites across the United States (AFCEE 1995). NA is achieved through the *in situ* destruction of contaminants by naturally occurring mechanisms, including destructive mechanisms such as biodegradation, abiotic oxidation, and hydrolysis, and nondestructive mechanisms such as sorption, dilution, and volatilization. The primary objective of this investigation is to determine whether natural attenuation will reduce contaminants in the groundwater to below regulatory standards before potential receptors are reached.

Fuel hydrocarbons biodegrade naturally when an indigenous population of hydrocarbon degrading microorganisms are present in the aquifer and sufficient concentrations of electron acceptors and nutrients are available for consumption by these organisms. The rate of natural biodegradation generally is limited by the amount of electron acceptors rather than by the amount of nutrients (e.g., ammonia, phosphate, nitrate) available. For this reason, comparison of the concentrations of the major electron acceptors (dissolved oxygen, nitrate, ferric iron, sulfate, and carbon dioxide) within fuel hydrocarbon plumes and at upgradient locations provides the basis for quantifying the biodegradation of fuel contaminants. Each of the major breakdown process and associated electron acceptors used to monitor the natural attenuation process are described below.

Aerobic Biodegradation. Dissolved oxygen is the first electron acceptor utilized during the biodegradation of dissolved fuel-contaminated water (AFCEE, 1995). Dissolved oxygen is thermodynamically favored and must be decreased to levels below 0.5 mg/L before anaerobic respiration is to occur.

Denitrification. Denitrification ultimately results in the formation of carbon dioxide, water, and dinitrogen gas (N_2). The absence of nitrate levels within a plume therefore suggests that nitrate may be functioning as an electron acceptor. While the oxidation of

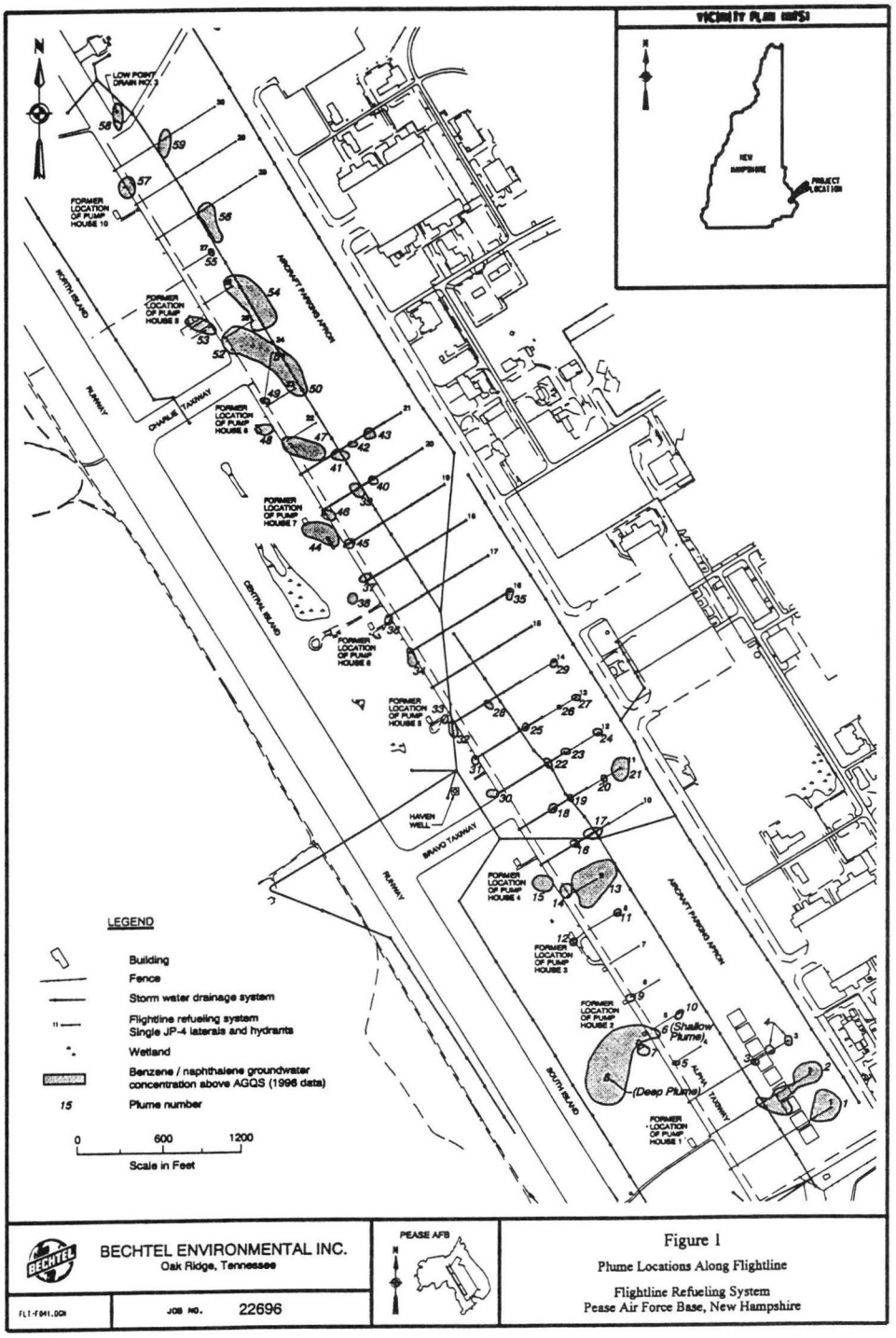

Figure 1

Plume Locations Along Flightline

Flightline Refueling System
Pease Air Force Base, New Hampshire

nitrate is thermodynamically more favorable than aerobic respiration, nitrate can only function as an electron acceptor in microbially facilitated BTEXN degradation reactions if anaerobic conditions exist (AFCEE, 1995).

Table 1. Natural Attenuation Processes (AFCEE, 1995)

Process	Reaction	Mass ratio[1]
Aerobic degradation	$C_6H_6 + 7.5\ O_2 \rightarrow 6\ CO_2 + 3\ H_20$	3.1:1
Denitrification	$6\ NO_3^- + 6\ H^+ + C_6H_6 \rightarrow 6\ CO_{2\,(g)} + 6\ H_20 + 3\ N_{2\,(g)}$	3.1:1
Iron (III) reduction	$30\ Fe(OH)_3 + 60\ H^+ + C_6H_6 \rightarrow 6\ CO_2 + 78\ H_20 + 30\ Fe^{2+}$	21.6:1
Sulfate reduction	$3.75\ SO_4^{2-} + 7.5\ H^+ + C_6H_6 \rightarrow 6\ CO_{2\,(g)} + 3\ H_20 + 3.75\ H_2S$	4.7:1
Methanogenesis	$C_6H_6 + 4.5\ H_20 \rightarrow 2.25\ CO_{2\,(g)} + 3.75\ CH_4$	0.7:1

[1]Mass of electron acceptor utilized or by-product produced per BTEXN destroyed.

Iron (III) Reduction. Once the available dissolved oxygen and nitrate have been depleted, iron (III) can be used as an electron acceptor (AFCEE 1995). During this process, insoluble iron (ferric iron) is reduced to soluble iron (ferrous iron,). The presence of elevated ferrous iron concentrations in the fuel hydrocarbon plume above upgradient levels suggests the biodegradation of dissolved fuel via iron reduction may be occurring.

Sulfate Reduction. Once the available oxygen and nitrate have been depleted from the aquifer matrix, sulfate-reducing bacteria become active (AFCEE 1995). Sulfate-reducing bacteria reduce sulfate to sulfide. Lower concentrations of sulfate measured within the plume compared to upgradient levels are therefore indicative of bioremediation. Sulfate reducing microorganisms typically are sensitive to environmental conditions, including temperature, inorganic nutrients, and pH. An imbalance in suitable environmental conditions can severely limit biodegradation of BTEXN through sulfate reduction.

Methanogenesis. Based on the free energy yield and the oxidizing potential, the CO_2-CH_4 redox couple can also be used to oxidize BTEXN to carbon dioxide and water (AFCEE 1995). This redox reaction is called methanogenesis, or methane fermentation. Methane fermentation yields less free energy to the system than the other chemical species. To attain necessary reducing conditions, other highly oxidizing chemical species such as oxygen and nitrate must be reduced first. The elevated levels of methane within the groundwater plume above upgradient levels suggests that biodegradation of the dissolved fuel may be occurring through methanogenesis.

3. FLIGHTLINE BACKGROUND NA PARAMETERS

Since NA relies on monitoring electron acceptor concentrations upgradient and within a plume, much emphasis was placed on calculating background concentrations along the flighline. For this effort, the flightline was separated into two zones: the area covered by grass ("grassy infield") and the area under the concrete parking apron ("parking apron"). The grassy infield is characterized by high recharge and hence has a much greater potential for replenishing depleted oxygen. Conversely, the groundwater underlying the parking apron receives only minor amounts of recharge (estimated to be 5 percent of the recharge

occurring over the grassy infield). Twenty-five wells were selected to determine background values: 14 from the grassy infield and 11 from the parking apron.

Dissolved Oxygen. As expected, dissolved oxygen concentrations varied greatly between the grass infield wells and parking apron wells. The grass infield wells had dissolved oxygen values ranging from 3.9 to 9.3 mg/L with an average value of 5.7 mg/L. Dissolved oxygen under the parking apron were all less than 1 mg/L with an average of 0.3 mg/L.

Nitrate. Nitrate values for both the grass infield and parking apron were similar, with averages of 13.5 and 9.7 mg/L, respectively. Nitrate levels varied significantly from to 0.05 to 80 mg/L. Elevated nitrate levels are due to activities that have previously occurred on the parking apron (e.g., deicing runway and taxiways urea).

Ferrous Iron. Background concentrations of ferrous iron in both grass infield and parking apron wells are low. Since ferrous iron is likely to be in the insoluble ferric iron form under high redox conditions, the ferrous iron measured in the grass infield wells were all low with the average being 0.12 mg/L. Background groundwater under the parking apron has lower redox potential with a higher average ferrous iron concentration of 1.8 mg/L.

Sulfate. Average background sulfate values for the grass infield and parking apron were 7.7 and 38.3 mg/L, respectively. The presence of higher sulfate levels under the parking apron is likely due to low recharge and corresponding sluggish groundwater circulation. Low groundwater velocities under the parking apron allow for longer residence times and therefore allow for the dissolution of other anionic species besides carbonates (i.e., sulfate and possibly chloride).

Methane. Methane background concentrations in areas upgradient from any source of contamination is generally not detected at 0.001 mg/L. The presence of methane, therefore, is a strong indication that methanogenesis is occurring.

Assimilative Capacity Calculation

An assimilative capacity was calculated for each plume that had permanent wells (plumes without permanent wells were identified during site investigations with using Geoprobe® sampling techniques). Table 2 summarizes the assimilative calculations on a plume-by-plume basis including the calculated assimilative capacity for oxygen, nitrate, ferrous iron, sulfate, and methane. These individual capacities are then summed to give a total assimilative capacity. From this data, it can be concluded that (1) the total assimilative capacity for each plume is greater than zero, indicating that natural attenuation is likely occurring at each of the plumes and (2) the individual assimilative capacities show that no one individual degradation process dominates over the entire flightline.

4. MODEL DEVELOPMENT

This section provides the development of the model for estimating the time for natural attenuation to reduce BTEXN concentrations to levels below the New Hampshire Ambient Groundwater Quality Standards (AGQSs). A simplified model was developed to estimate remediation times due to the large number of contaminant plumes along the

Table 2. Assimilative Capacity and Natural Attenuation Calculation Summary

Plume	Observed Change (Δ) in Parameter (mg/L)					Total A.C (mg/L)	Total BTEXn (mg/L)	Hydaulic Gradient (ft/ft)	Hydraulic Conductivity (ft/day)	Plume Length (ft)	Cleanup Time (years)
	Oxygen	Nitrogen	Fe (II)	Sulfate	Methane						
1	0.1	0.2	54.9	21.0	NS	6.9	32.8	0.003	2.1	50	178.
2	0.0	7.9	98.2	33.3	1.6	15.1	1.0	0.008	2.1	400	7.46
3	0.0	1.9	5.8	29.7	0.3	7.3	1.5	0.002	2.1	70	15.3
4	0.0	8.5	5.7	23.4	0.0	7.0	4.4	0.002	2.1	90	56.5
5	3.9	5.6	2.2	0.0	0.0	2.5	BTEXn < Cleanup Goals in Fall '96				NC
6	5.3	12.8	41.9	0.0	0.0	6.3	21.9	0.0013	1.2	150	1610.
7	5.7	2.5	0.0	0.0	NS	2.4	0.7	0.001	1.2	40	1.93
8	5.5	13.4	72.9	6.7	0.0	9.3	10.9	0.0004	32.6	600	438.
9	4.9	13.4	2.1	4.2	0.0	5.4	11.6	0.002	1.2	90	373.
10	0.0	8.3	0.0	31.5	0.0	8.3	BTEXn < Cleanup Goals in Fall '96				NC
12	NS	10.0	3.4	0.0	NS	2.3	0.2	0.002	5.7	40	0.05
13	0.0	9.0	5.4	32.9	0.0	9.1	6.4	0.005	5.7	200	23.8
14	NS	13.5	119.9	6.7	0.2	9.9	14.4	0.007	5.7	75	13.1
15	5.4	13.2	0.1	0.0	NS	4.5	BTEXn < Cleanup Goals in Fall '96				NC
16	0.2	0.0	5.4	0.0	0.0	0.3	BTEXn < Cleanup Goals in Fall '96				NC
17	0.0	0.0	18.8	16.0	1.0	5.5	5.0	0.001	0.5	80	771.
18	0.3	9.1	0.0	0.0	0.2	2.3	BTEXn < Cleanup Goals in Fall '96				NC
19	0.1	9.3	0.0	0.0	0.0	2.0	BTEXn < Cleanup Goals in Fall '96				NC
21	0.2	9.4	46.1	27.2	4.7	15.8	3.8	0.006	0.5	120	46.2
22	0.2	9.3	5.3	15.3	0.2	5.8	BTEXn < Cleanup Goals in Fall '96				NC
24	0.0	9.0	118.2	0.0	3.3	11.4	0.3	0.007	0.5	70	0.32
25	0.1	7.5	0.0	22.3	0.0	6.3	BTEXn < Cleanup Goals in Fall '96				NC
27	0.1	9.3	9.2	32.4	1.9	11.6	1.3	0.006	0.5	100	16.7
28	0.1	8.9	5.0	25.3	0.0	7.4	2.7	0.004	0.5	90	73.7
29	0.2	9.3	4.3	33.6	0.1	9.4	5.8	0.004	0.5	70	85.9
30	5.7	0.0	2.6	0.0	NS	1.9	0.2	0.008	12	110	0.22
31	5.4	0.0	0.0	0.0	NS	1.7	0.5	0.007	12	50	0.17
32	5.5	6.5	5.4	3.9	NS	4.2	0.0	0.006	12	50	0.07
33	1.7	0.0	0.0	0.0	0.2	0.8	BTEXn < Cleanup Goals in Fall '96				NC

Table 2. Assimilative Capacity and Natural Attenuation Calculation Summary

Plume	Observed Change (Δ) in Parameter (mg/L)					Total A.C (mg/L)	Total BTEXn (mg/L)	Hydaulic Gradient (ft/ft)	Hydraulic Conductivity (ft/day)	Plume Length (ft)	Cleanup Time (years)
	Oxygen	Nitrogen	Fe (II)	Sulfate	Methane						
34	5.0	0.0	1.6	5.6	1.4	4.6	1.7	0.005	12	130	3.18
35	0.2	6.2	2.6	33.7	0.0	8.6	1.2	0.006	21.8	100	0.23
36	5.6	13.5	2.3	0.0	0.4	5.2	BTEXn < Cleanup Goals in Fall '96				NC
37	5.3	0.0	0.0	0.9	0.1	2.0	0.0	0.007	12	100	0.32
38	0.2	11.1	0.0	0.0	0.0	2.4	BTEXn < Cleanup Goals in Fall '96				NC
39	0.2	0.0	0.0	36.5	0.0	7.7	2.1	0.015	11.5	170	1.19
40	0.1	0.0	7.4	28.3	0.0	6.3	0.1	0.007	11.5	110	0.
41	NS	15.4	0.1	0.0	0.0	3.3	13.9	0.019	11.5	140	13.2
43	0.2	1.2	0.0	34.0	0.0	7.4	0.3	0.005	32.8	120	0.5
44	3.9	0.0	12.9	0.0	0.2	2.0	0.9	0.016	6	170	2.13
46	NS	13.4	35.9	5.6	0.6	6.4	1.6	0.018	6	110	0.99
47	3.3	9.6	72.9	0.8	0.5	7.2	6.0	0.019	11.5	230	4.62
48	5.5	9.3	71.9	4.9	0.9	9.2	19.6	0.004	116.2	120	2.47
49	5.5	2.5	0.5	0.0	0.0	2.3	1.0	0.012	11.5	210	3.74
50	0.3	0.9	0.0	37.3	NS	8.1	0.4	0.015	11.5	250	0.63
51	0.2	26.8	26.9	0.0	NS	6.9	6.5	0.01	11.5	140	5.48
52	5.2	0.0	26.9	0.7	0.7	3.9	3.9	0.005	13.2	240	20.1
53	3.7	5.7	8.4	0.0	0.5	3.4	5.9	0.004	13.2	120	0.86
54	0.1	4.6	39.2	27.3	0.0	8.5	10.8	0.004	13.2	470	2.38
56	0.4	28.8	59.3	21.0	NS	13.2	13.7	0.0007	13.2	310	167.
57	5.0	13.5	21.9	6.7	0.0	6.8	4.7	0.002	13.2	110	11.2
58	0.5	0.1	59.8	5.6	NS	4.0	1.7	0.003	13.2	120	6.76
59	9.1	1.0	28.9	0.0	NS	4.4	2.5	0.006	13.2	130	3.98

Plumes 11, 20 ,23, 26, 42, 45, 55, 60 do not have permenent wells and were not included in calculations (no Fall 1996 samples were taken)

Cleanup times were not calculated for plumes which did not have cleanup goals exceeded in Fall 1996

Obseved changes (Δ) calculated by determining difference between upgradient (background) and source concentrations

A.C = Total Assimilative Capacity = ΔOxygen/3.1+ΔNitrogen/3.1+ΔFe(II)/21.6+ΔSulfate/4.7+ΔMethane/0.7

BTEXn = benzene, toluene, ethylbenzene, xylenes, and naphthalene; NS = not sampled; NC = not calculated

flightline and also due to the uncertainty associated with the source history and time and size of the release. This approach calculates the remediation time based on the rate-limiting characteristic of the plume: either rate limiting microbial kinetics or availability of electron acceptors.

The first type assumes that electron acceptors are in surplus and that the reaction is rate-limited by microbial kinetics. The second model assumes that microbial kinetics are relatively fast ("instantaneous") and that the transport of electron acceptors via groundwater recharge is rate-limiting. Information presented by EPA (1996) shows that in most instances the second model type is applicable to modeling natural attenuation of dissolved petroleum hydrocarbons.

Data gathered from two of the flightline plumes studied in detail, show that at one plume, the transport of electron acceptors is rate limiting while at the other, microbial kinetics are rate limiting. For the remaining plumes, not enough information was available to determine which rate-limiting model was correct. Therefore, two separate calculations were performed, one for microbial limited rates and the second one for electron acceptor limited rates. The slower of the microbial limited rate and electron acceptor limited rate was assumed to be the rate-limiting process. Calculations for each are described below.

Microbial Limited Calculations. For the derivation of the microbial limited calculation, consider a control volume containing the contaminant plume. Assuming that this control volume can be treated as a continuous-flow stirred-tank reactor, a mass balance of the dissolved phase hydrocarbons can be written as follows:

$$VR_i \frac{dC_i}{dt} = \left(QC_i\right)_{in} - \left(QC_i\right)_{out} - \left(V\lambda_i\right) \quad (1)$$

where: V = control volume surrounding the plume (ft^3); R_i = retardation coefficient of solute i (unitless); C_i = concentration of solute i (µg/L); Q = volumetric flow rate (ft^3/yr); λ_i = first order decay coefficient of solute i (yr^{-1}). The first term accounts for the change of dissolved hydrocarbon concentration over time, with the retardation coefficient accounting for partitioning between the dissolved phase and sorbed phase. The next two terms account for the mass flux of dissolved hydrocarbon into and out of the control volume, respectively. The last term represents the biological decay of the dissolved hydrocarbon.

For this calculation, the mass flux of hydrocarbon into the control volume is assumed to be zero. The mass flux of hydrocarbon is also assumed to be zero. This is a conservative assumption that states that there is no mass loss due to advection (only biological decay accounts for mass loss in the control volume). Setting the second and third term to zero and solving for C yields the following equation:

$$C = C_O e^{-\frac{\lambda}{R}t} \quad (2)$$

The time to reach the AGQS is then:

$$t_{AGQS,i} = -\frac{R}{\lambda}\ln\left(\frac{C_{AGQS,i}}{C_{O,i}}\right) \quad (3)$$

where $C_{AGQS,i}$ = ambient groundwater quality standard of solute i (µg/L); $C_{O,i}$ = present concentration of solute i (µg/L); $t_{AGQS,i}$ = time to reach AGQS (yr). Remediation times

are calculated for each plume where AGQSs were exceeded. Remediation times were calculated based on maximum current concentrations and a published half-lives.

Electron Acceptor Limited Calculation. Electron acceptor depletion is dependent on the groundwater seepage velocity through the plume. The "instantaneous" reaction assumes electron acceptors are immediately depleted upon entering the contaminated regions. The dissolved hydrocarbons concentrations are then reduced proportionally with respect to the reduction in electron acceptors or increase in byproducts, with the reduction being based on the stoichiometric relationship presented in Table 1.

For the derivation of the electron acceptor limited calculation, consider a control volume placed around the contaminant plume with a length equivalent to the existing plume length. Assuming that this control volume can be treated as a continuous-flow stirred-tank reactor, a mass balance of the dissolved phase hydrocarbons can be written as:

$$RV\frac{dC_i}{dt} = (QC_i)_{in} - (QC_i)_{out} - \left(Q\sum_j f_i\left(F_j \times \Delta EA_j\right)\right) \quad (4)$$

where: f_i = mass fraction of hydrocarbon i to total BTEXN (mg/mg); F_j = stoichiometric factor between electron acceptor and hydrocarbon (see Table 1); ΔEA_j = difference between upgradient and plume electron acceptor/byproduct concentrations (mg/L). The first term accounts for the change of dissolved hydrocarbon concentration over time, with the retardation coefficient accounting for partitioning between the dissolved phase and sorbed phase. The next two terms account for the mass flux of dissolved hydrocarbon into and out of the control volume. The last term represents the "instantaneous" reaction based on assimilative capacity of the upgradient groundwater.

As was done in the microbial limited equation, the flux into and out of the control volume is set to zero. This is conservative and simply states that the current mass of hydrocarbons within the control volume can only be degraded as fast as the electron acceptors can be replenished (i.e., no losses due to advection or dispersion). Setting the second and third term to zero and solving for C, (4) becomes:

$$C_i - C_{AGQS,i} = \frac{1}{RT}\left(f_i\sum_j\left(F_j \times \Delta EA_j\right)\right)t_{AGQS,i} \quad (5)$$

where T= hydraulic detention time (yr) = (V/Q). The hydraulic detention time is the average time it takes to remove one groundwater pore volume. The hydraulic detention time can be calculated by dividing the control volume by the steady-state flow through the control volume, or:

$$T = \frac{V}{Q} = \frac{l \times w \times h}{v_s \times w \times h} = \frac{l}{v_s} \quad (6)$$

Where l = length of the plume (ft); v_S = groundwater seepage velocity through the control volume (ft/yr). Substituting (6) into (5), the time to reach AGQS, assuming electron acceptor limited reaction, is then:

$$t_{AGQS,i} = \frac{\left(C_{o,i} - C_{AGQS,i}\right)RT}{f_i\sum_j\left(F_j \times \Delta EA_j\right)} \quad (7)$$

5. MODEL RESULTS

Remediation times were calculated for each of the plumes that had dissolved petroleum hydrocarbon AGQS exceedances (Table 2). Eleven of the original 60 plumes did not have any BTEXN AGQS exceedances, based on the fall 1996 sampling results, and were not included in the calculations. Eight of the original 60 plumes do not have permanent monitoring wells and were also not included in the calculations.

Calculations for both models were performed for each of the dissolved hydrocarbon constituents that had AGQS exceedances. This list included benzene, toluene, ethylbenzene, xylenes (total), and naphthalene. To be conservative, the maximum detected value of each constituent within that plume was used. Therefore, the mass fraction of the individual constituents (f_i) was calculated using the maximum concentrations divided by the sum of the maximum BTEXN compounds.

Table 2 also summarizes the plume characteristics including maximum concentrations of BTEXN, assimilative capacity, seepage velocity, and plume length. Site specific and literature data were to calculate retardation factors and determine decay coefficients. Due to the number of assumptions that went into developing these models, plumes are grouped into estimated cleanup time ranges. Time ranges to reach AGQS were arbitrarily divided into three categories: <5 years (fast), 5–50 years (moderate), >50 years (slow). Out of the 60 original plumes along the flightline, 11 no longer have any BTEXN AGQS exceedances (19 percent), 21 have estimated attenuation times of less than 5 years (35 percent), 11 have attenuation times between 5 and 50 years (18 percent), and 9 have attenuation times greater than 50 years (15 percent). Eight of the plumes (13 percent) had no permanent wells and were not included in the calculations.

6. SUMMARY

- **Natural attenuation of dissolved petroleum hydrocarbons has been documented in petroleum hydrocarbon plumes along the flightline at Pease AFB.** Assimilative capacities for each plume range from 0.3 to 15.0 mg/L, with the median capacity being 6.3 mg/L. Total BTEXN concentrations at these plumes range from not detected to 32.5 mg/L with the median concentration being 1.3 mg/L.
- **Over 50 percent of the plumes are estimated to be below AGQS within 5 years.** The initial site investigations characterized 60 dissolved hydrocarbon plumes along the flightline with AGQS exceedances. Based on the fall 1996 sampling results, 11 plumes no longer have any BTEXN AGQS exceedances and 21 plumes are estimated to be below AGQS within 5 years.
- **Dissolved oxygen, nitrate, ferrous iron, sulfate, and methane are all active participants in the NA process.** No single electron acceptor/metabolic byproduct is dominant along the flightline. Average assimilative capacities for these parameters are: 0.7, 1.5, 1.0, 2.5, and 0.5 mg/L, respectively.

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Application of Geochemical Prospecting and Exploratory Data Analysis Methods on Data from Contaminated Sites by PAHs.

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Keywords : data analysis, characterisation, behaviour of contaminants, PAH, soil and groundwater contamination

SUMMARY

Characterisation of pollutions at former industrial sites is generally carried out following a case by case approach based on the results of site investigations and the modelling of fate of present pollutants. Both can be rather delicate because of the heterogeneity in pollutants and environmental characteristics. A *systemic* or *macroscopic* approach of soil pollution, based on exploratory data analysis (EDA) on existing sites, might contribute to capitalisation of information and optimisation of studies. This paper presents results of an EDA on PAH on former gas and coking plants in France, Germany and the Netherlands.

RESUME

La caractérisation de pollutions sur des anciens sites industriels est généralement effectuée selon une approche au cas par cas, basée sur les résultats des investigations sur le site et éventuellement la modélisation du devenir des polluants présents. Ces deux étapes s'avèrent souvent délicates pour des raisons d'hétérogénéité aussi bien des polluants que des caractéristiques de l'environnement. Une approche systémique, basée sur l'analyse exploratoire de données (EDA) sur des sites existants peut contribuer à la capitalisation d'information et d'expertise. Ce papier présente les résultats de l'analyse exploratoire appliquée aux données de pollutions par HAP générées par des activités de gazéification de charbon sur des anciens sites d'usines à gaz et de cokeries en France, en Allemagne et aux Pays-Bas.

Contaminated Soil '98, Thomas Telford, London, 1998, 213–219

INTRODUCTION

The characterisation of soil pollution, the risk assessment and the definition of eventual reclamation actions and -goals are principally based on the results of sampling campaigns in soil and ground water. However, these campaigns of data gathering are delicate, due to heterogeneity in pollutions and in environmental characteristics, and the difficulties associated to guarantee representativity in sampling and chemical analysis. From a pragmatic point of view, we observe that sampling is generally quite onerous; Data on individual sites are therefore often in limited quantity.

Besides these difficulties associated to the *identification* of the pollution, the *modelling of the fate* of pollutions shows to be very complex. In general, one would not have information on every relevant parameter. Furthermore, processes governing the fate of pollutions are numerous and very complex and field situations, the role of each of the parameters as well as the mutual interferences are difficult to simulate in a model. Although important scientific advances have been made, the fate of pollutants is still difficult to predict, and those of *mixtures* of pollutants even more.

These difficulties are not exclusively associated to polluted sites: other fields of earth sciences are exposed to these as well. In geochemical prospecting, aimed at the exploitation of -often hidden- ore bodies, a methodology is elaborated. It is based on exploratory data analysis (EDA) by means of statistical tools of voluminous collections of field data on environmental characteristics and concentration levels (Rose et al., 1979).

It aims at the determination of concentration ranges, typical for different geogenous conditions, and characteristic associations of elements. It has proved its interest in the field of geochemical prospecting, and might as well contribute to an optimisation of studies on polluted sites, both by inducing a reduction of parameters to identify and by improving the understanding of pollutions in the environment as a *system*, rather than the modelling of each process individually. It might thus offer a complement to the actual case by case studies on industrially polluted sites.

The methodology has primarily been tested on data of Polycyclic Aromatic Hydrocarbons (PAH) pollutions generated by manufactured gas plant (MGP) sites and coking plants. These pollutions show generally low mobility towards air and ground water, and prove to be persistent in the environment (Thomas and Lester, 1994). Several compounds, like benzo(a)pyrene, have carcinogenic activities and are therefore pollutants of interest in risk assessment studies (IARC, 1984).

The present paper describes (a) the definition of typical pollution indices for MGP and coking plant site pollution by PAH in tars and (b) the existence of indicator compounds in the family of PAH, allowing to predict concentration levels of other PAHs on the site.

THE DATA ON PAH POLLUTIONS

Data from 45 site investigation studies[1] have been collected in France, Germany and the Netherlands and captured in a database. All studies are recent (>1990) and results are based on comparable sampling methods and chemical analysis (Soxhlet extraction and either GC or HPLC identification of 16 PAH-compounds (EPA, 1993)).
The data base contains data on 2578 soil samples. In some points, PAH are below detection limit or not analysed; this lack of information is coded by 'NA' in the database. Multivariate analysis does not support missing data ('NA') and concerns only those sampling points where information on relevant parameters is available.

Generally, data sampling campaigns concern above all areas with potentially high contamination levels (identified in studies on industrial history at the site). The results of the present study will thus generally reflect the situation at polluted areas on a site, and are not necessarily representative of the polluted sites as a whole.

METHODOLOGY OF THE STUDY

The programming environment Splus on UNIX platform is used for exploratory analysis of data on concentration levels in the sampling points at the sites. The study is based on relatively simple statistic data treatment techniques, while these will put to the evidence the most important population characteristics. More sophisticated methodologies will only add few to the understanding of a data set on environmental contexts (Sinclair, 1989). Furthermore, statistical prerogatives are not always explicitly met in earth sciences (Davis, 1986), and this can generate lack of statistic stability of results.

EXPLORATORY DATA ANALYSIS.

Prior to any EDA, one has to identify the principal statistical characteristics of the populations related to each of the industrial activities. Each of the PAH compounds showed a Gaussian distribution pattern in concentration levels after logarithmic transformation, with typical mean values between -0.35 (0.45 mg/kg) for dibenzo(ah)anthracene and 0.50 (3 mg/kg) for pyrene. Variance is important, especially for relatively light PAH and varies from 2.132 (naphtalene) to 0.77 (dibenzo(ah)anthracene). Statistical significant differences (t-test, $\alpha = 0.05$) have been observed for the light PAHs (naphtalene, acenaphtene, acenaphtylene, fluorene, phenanthrene, and anthracene) between coking plant sites on the one hand and MGP on the other (Oosterbaan and Jamet, 1997). This difference can be exploited in order to define typical characteristics for both PAH pollutions.

The following EDA are based on logtransformed concentration levels, in order to study populations with gaussian behaviour. Furthermore, we will obtain expressions

[1] the database contains data on 17 coking plants and 28 MGP sites.

in terms of *orders of magnitude* rather than absolute values, which is more relevant in environmental studies, and more reliable with regard to incertitude in sampling practices and chemical characterisation of the analytes.

THE DISTINCTION OF INDUSTRIAL ORIGIN OF A PAH-POLLUTION BY 'INDICES'.

One of the opportunities offered by EDA is the identification of typical 'indices' for pollutions, like exclusive signatures of a polluted context. In studies on hydrocarbons in oil prospecting, this approach has offered parameters allowing a rapid characterisation of the origin of the presence of hydrocarbons. It indicates whether one faces pyrolytic, petrologic, biogenetic or diagenetic hydrocarbons. These 'indices' are generally based on a relation between two compounds in a mixture. One of the indices identified the study on petrol is the ratio of concentration levels of phenanthrene vs. anthracene in a solid medium. The difference in angular stability between these two compounds makes that values of this index are generally beyond 25 if the PAH mixture is of petrologic origin, and below 10 for pyrolytic origins (Bouchez et al., 1997). This verifies for the MGP and coking plant pollutions studied in the present research program. In both cases, the mean value is far below 10 (4.8 for MGP and 5.4 for coking plant pollutions).

With regard to the composition of PAH-mixtures in soils at coking plant sites and at MGP sites, the fractions of anthracene and phenanthrene showed both to be higher in coking plant pollutions: an average PAH pollution (sum of 16 PAHs) contains 8% of anthracene and 25% phenanthrene on coking plant sites; this is less than 5% and nearly 15% for the same compounds in MGP site pollution. Therefore, indices aiming at distinction between the two pollution types may be based both on anthracene and on phenanthrene. These are studied in relation to the benzo(a)pyrene one of the most toxic PAHs with a high predicting capacity (see second part). Statistic stability is obtained after logtransformation, so in fact we measure the difference of logarithmic concentration levels :

$$I_{Phe\,/\,Bap} = \left(\log[_{phenanthrene}] - \log[_{benzo(a)pyrene}]\right)$$

		min	1st Q	Med	Mean	3rd Q	max	var.	N
I_{PheBap}	MGP	-1.74	-0.22	0.06	0.17	0.52	2.2	0.30	958
	Coking P	-1.06	0.07	0.48	0.58	1.12	2.14	0.46	239
I_{AntBap}	MGP	-1.71	-0.81	-0.46	-0.39	0	1.85	0.32	839
	Coking P	-1.89	-0.48	-0.03	-0.02	0.39	0.40	1.72	220

Table 1. Statistical characteristics of calculated indices on soil pollution at 28 MGP and 17 coking plant sites in Europe, based on the ratio of concentration levels of two compounds in all sampling points (log mg/kg).

Table 1 gives the statistical characteristics observed in our data population for the two indices. Statistical t-test confirmed that the differences between the pollutions generated by MGP and coking plants are significant (α= 0,05, d.f. 1195 and 1057).

So both for I_{PheBap} and I_{AntBap} values on coking plants are higher. In order to evaluate whether these indices are exclusive, e.g. typical, further research has to focus on a third industrial activity generating PAH pollutions, and on more data concerning the actual pollutions.

PREDICTION OF CONCENTRATION LEVELS BY INDICATOR COMPOUNDS.

The visual analysis of relation between the concentration levels of PAHs in soil sampling points after logarithmic transformation shows high linear correlations for most of the heavy PAH compounds, both in MGP pollutions and coking plant pollutions. These results are described more in detail in Oosterbaan and Jamet (1997). This strong correlation between concentration levels suggests the existence of indicator substances, substances whose chemical analysis can give valuable information on the concentration levels of other compounds in an identical context. Multivariate linear regression is applied, based on a maximum of 3 explicative parameters for the prediction of concentration levels of 13 other PAHs. For toxicological considerations, we have been studying the predicting capacity of benzo(a)pyrene, the most carcinogenic PAH compound identified until now (IARC, 1984). Light PAH not showing high correlation with this compound, fluoranthene has been retained, considering it as an intermediate compound as well as naphtalene, the lightest PAH.

MGP pollution	n	intercept	NAP	FLN	BAP	R^2
ACY	310	-0.63	0.53	-	0.51	79%
ACE	353	-0.58	0.48	0.41	-	69%
FLU	614	-0.62	0.44	0.62	-	84%
PHE	395	-0.08	0.23	0.83	-	92%
ANT	654	-0.73	0.19	0.91	-	91%
PYR	439	0.06	-	0.69	0.31	98%
CHR	615	-0.02	-	-	0.99	96%
BaA	618	0.03	-	-	1.01	97%
BbF	334	0.07	-	-	0.95	97%
BkF	533	-0.26	-	-	0.97	97%
BgP	308	-0.18	-	-	0.92	95%
IP	604	-0.12	-	-	0.92	96%
DahA	601	-0.66	-	-	0.86	87%

Table 2. Multivariate linear regression with 3 explicative variables - logarithmic soil concentration levels of naphtalene (NAP), fluoranthene (FLN) and benzo(a)pyrene (BAP) (log mg/kg dry matter) - for prediction of 13 other PAH concentration levels on 28 MGP sites. n = number of sampling points concerned, R^2 = percentage of variance explained by explicative variables.

Results of multivariate regression with these three compounds in the prediction of 13 others are resumed in tables 2 and 3. They show that in the case of these 45 polluted sites, the determination of only three out of 16 PAH allows satisfactory

prediction of logarithmic concentration levels of the rest of the compounds in the PAH pollution mixture (predicted concentration levels at about 70% to 98% of identified logtransformed concentrations). Both on MGP and on coking plant sites, the prediction is based on naphtalene and fluoranthene concentration levels for PAH composed of less than 4 benzene cycles[2], and only on those of benzo(a)pyrene for the heavy PAH, e.g. 4 cycles or more. These compounds can be designed by 'indicator compound'. The existence of such indicator compounds allows a reduction of chemical analyses on the sites. In the present case of PAH pollutions, this might be of moderate interest - the chemical analysis of 16 PAH compounds is not five times as complicated and onerous as the analysis of only three of them. Nevertheless, it proves the feasibility of a macroscopic and systemic approach and the possible contribution of this methodology in soil pollution studies. Furthermore, these findings can guide phenomenological studies on pollutants. The study of the fate of a PAH-pollution in a soil helps the determination of two subcategories of PAH, the compounds in each category presenting comparable characteristics.

Coking Plant pollution	n	intercept	NAP	FLN	BAP	R^2
ACY	122	-0.67	0.32	-	0.79	75%
ACE	151	-0.36	0.33	0.61	-	54%
FLU	165	-0.30	0.39	0.63	-	67%
PHE	183	0.13	0.23	0.86	-	87%
ANT	175	-0.39	0.21	0.70	0.18	86%
PYR	174	-0.05	-	0.68	0.32	97%
CHR	172	0.23	-	-	0.97	94%
BaA	171	0.23	-	-	0.99	94%
BbF	62	0.16	-	-	1.00	89%
BkF	55	-0.26	-	-	0.95	88%
BgP	135	-0.18	-	-	0.94	90%
IP	159	-0.16	-	-	0.90	91%
DahA	158	-0.58	-	-	0.90	86%

Table 3. Multivariate linear regression with 3 explicative variables - logarithmic soil concentration levels of naphtalene (NAP), fluoranthene (FLN) and benzo(a)pyrene (BAP) (log mg/kg dry matter) - for prediction of 13 other PAH concentration levels on 17 Coking Plant sites. n = number of sampling points concerned, R^2 = percentage of variance explained by explicative variables.

CONCLUSION

This study shows the contribution of a macroscopic, systemic approach in the characterisation of a PAH pollution on industrial sites. By the definition of typical 'indices' based on the ratio of logarithmic concentration levels, one can separate pollutions in soil generated by coking plants from those resulting from MGP sites. Both I_{PheBap} and I_{AntBap} show higher mean values on coking plant sites (0.5 and 0 instead of 0.1 and -0.4). Multiple regression shows on the one hand that the analysis of only 3 so-called 'indicator-substances' can offer satisfactory prediction capacity for the concentration levels of 13 other PAH, and can offer aid in phenomenological

[2] The minimum scores are obtained in case of acenaphtene, which is known for the difficulties in analytical detection.

studies on the other hand by the distinction of two subcategories of PAHs, each of them having a specific pollution pattern.

ACKNOWLEDGEMENT

Thanks are due to the French Agency for Environment and Energy Management (ADEME) for the support of this research project and to the providers of data: ADEME, Gaz de France and DRIRE, in France; provincial services and Heidemij in the Netherlands and environmental agencies NordRhein-Westfalen and Baden-Württemberg, Germany.

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MEASUREMENT UNCERTAINTY ARISING FROM SAMPLING CONTAMINATED LAND: A TOOL FOR EVALUATING FITNESS-FOR-PURPOSE.

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Keywords: Sampling methods, quality control, reliability sampling, cost-benefit analysis, classification.

SUMMARY

New methods have recently been devised to estimate the uncertainty in measurements caused by the processes of both sampling and chemical analysis. Knowing this uncertainty, allows judgements to me made as to whether a sampling protocol is appropriate, based on a fitness-for-purpose criteria such as an acceptable level of uncertainty. A fundamental change in sampling philosophy is thereby to encourage the use of a range of appropriate sampling protocols that give estimates of uncertainty, rather than to pursue the use of a single uniform protocol, to give measurements of acceptable quality.

KURZFASSUNG

Es wurden in letzter Zeit Methoden zur Abschätzung der durch das Probenahme- sowie das chemische Analyseverfahren verursachten Meßungenauigkeit entwickelt. Wenn diese Ungenauigkeit bekannt ist, kann aufgrund entsprechender Kriterien, wie z.B. ein annehmbarer Ungenauigkeitsgrad, beurteilt werden, ob eine Beprobungsstrategie angemessen ist. Es stellt daher eine grundlegende Neuerung in der Probenahmephilosophie dar, zur Abschätzung der Meßungenauigkeit und um Daten entsprechender Güte zu erhalten, die Anwendung einer Reihe angemessener Beprobungsstrategien zu fördern, statt sich auf eine allgemeine Strategie festzulegen.

RÉSUMÉ

De nouvelles méthodes ont été conçues récemment pour estimer l'incertitude sur les mesures, causée par deux procédés: le prélèvement d'échantillons et l'analyse chimique. La connaissance de l'incertitude permet de juger si le protocole de prélèvement est adéquate, d'après un critère d'adaptation pour le but, pour aboutir à un niveau d'incertitude acceptable. Par conséquent, pour donner des résultats acceptables, il faut changer la philosophie du prélèvement: il est recommendé d'utiliser un certain nombre de protocoles qui estiment l'incertitude plutôt que de continuer à n'en utiliser qu'un seul.

Contaminated Soil '98, Thomas Telford, London, 1998, 221–230

INTRODUCTION

A mistaken emphasis in contaminated land sampling has often been the pursuit of the perfect sampling protocol. A more useful approach is to estimate the measurement uncertainty caused by whatever sampling protocol is employed. A decision can then be made on whether this level uncertainty is acceptable; and therefore whether the protocol and measurements are fit-for-purpose. This approach allows the design and cost of a protocol to be made appropriate for the particular situation at a specific site. There are situations for which a relatively large measurement uncertainty is acceptable, and a simple low-cost protocol will suffice. There are other situations however, when the cost of misclassifying the land is so high, that measurement uncertainty must be reduced to a low level. This will require a high-cost protocol that includes a method for estimating the uncertainty with a high degree of confidence.

This paper explains the meaning of measurement uncertainty and reviews methods that have recently been developed for the estimation of this measurement uncertainty caused by both field sampling and chemical analysis [1]. These methods range in complexity from the simple taking of some samples in duplicate [2], to the use of several samplers applying different sampling protocols at the same site [3]. Application of these methods are described, and a comparison made between the different methods. Measurement uncertainty is considered as a fitness-for-purpose criterion, either in comparison with the geochemical variance across a site for that analyte, or as part of cost-benefit analysis.

WHAT IS MEASUREMENT UNCERTAINTY?

Uncertainty in measurement has become an important issue in chemical analysis [4,5,6]. In many ways it draws together many concepts from analytical quality control (AQC) and focuses on the most important issue, which is the uncertainty of the measurements, rather than the quality of the analytical system. It also enables a change in emphasis away from the traditional question 'is this measurement system in control?' to the more relevant 'what is the uncertainty on this particular measurement?'. This leads on to the possibility that the uncertainty information can be carried with the concentration value into the interpretation of the measurement, rather than being left in an AQC system.

The International Standards Organisation (ISO) define uncertainty as 'A parameter associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand'[4] . A less formal, but perhaps more understandable description of measurement uncertainty, is that it is 'the interval around the result of a measurement that contains the true value with high probability'[7]. The standard uncertainty 'u', can be considered equivalent to one standard deviation which is often used to describe a normally distributed error. The expanded uncertainty 'U' is equal to the product of the standard uncertainty and a coverage factor 'k', which typically has a value of 2 of 3. This is analogous to the use of multiples of standard deviation for the quantification of precision. In the formal definition, systematic errors are not included in estimates of uncertainty, but only any residual random errors left after the correction of the systematic errors. However, the distinction between systematic and random errors in this application becomes blurred. The systematic error of one sampler becomes a random error when assessed as part of a multi-sampler comparison. In this approach systematic errors (such as sampling bias) do become incorporated in estimates of uncertainty.

METHODS FOR ESTIMATING MEASUREMENT UNCERTAINTY ARISING FROM SAMPLING.

Two type of method have been described for the estimation of uncertainty from analytical methods, which can be broadly described as 'bottom up' and 'top down'. In the 'bottom up' method, an error budget is drawn up of all the possible sources of uncertainty, each contribution estimated experimentally, and the total calculated from the sum of the squares [4,5]. The limitations of this method are that, it requires a great deal of effort to implement properly and even then, not all sources of uncertainty may be recognized. Inexperienced practitioners always tend to underestimate the uncertainty by this method. The 'top-down' approach uses the measurements from inter-organisational trials to give an estimate of the uncertainty[6]. This includes the bias between different organisations, that is often overlooked in the bottom-up method.

One limitation with both of these methods is that they ignore any uncertainty that is generated in the process of field sampling. If a sample is perfectly representative of the sampling target from which it is taken, then it will not contribute to the measurement uncertainty. Samples taken from the environment, and particularly those taken from contaminated land, are however never perfectly representative. Repeated sampling using the same protocol has shows that there are random errors that contribute to the uncertainty [2]. In addition, each sampling protocol and each individual sampler can introduce systematic errors in the form of sampling bias [8]. All of the concepts for the estimation of analytical quality (including uncertainty) can be applied to the estimation of sampling quality [9]. Overall measurement uncertainty can therefore be considered to arise from four sources, which are sampling bias, analytical bias, sampling precision and analytical precision. The analytical precision and bias are often measured, but the measurements rarely leave the AQC scheme. The measurement of sampling precision has been advocated for many years [10] but is rarely applied. Sampling bias has rarely been estimated [8] and even its existence has been denied by some workers, when a 'correct' sampling is applied [11].

Four methods have been devised recently for the estimation of uncertainty from both sampling and chemical analysis, and have been applied to the measurement of contaminated land [1]. They differ in the number of sampling personnel (i.e. samplers) and the number of sampling protocols applied. These methods are for: (1) single sampler/ single protocol, (2) single sampler/ multiple protocols, (3) multiple sampler/ single protocol, and (4) multiple sampler/ multiple protocols.

The simplest methodology for estimating sampling and analytical precision (Method 1) involves the taking of duplicate samples at some proportion of the sampling locations. For single increment samples, this proportion would typically be at 10% of the sampling locations [2]. These duplicate samples are not taken at exactly the same position as the original, but displaced by a distance representative of the possible uncertainty in interpreting the sampling protocol. For spatial surveys the distance between duplicate sampling locations will depend on the particular surveying technology employed. Where composite samples are taken this will require the duplication of the whole procedure at some locations (e.g. 10%). The protocol may leave unspecified the orientation of the sampling design, or the starting point[12], so the taking of the duplicate sample should reflect the effect of such different interpretations of the protocol.

Despite being basically a 'top-down' approach, the separation of the uncertainty caused by the chemical analysis from that caused by the sampling can be made by using a balanced experimental design. This requires duplicate analyses to be made on both of the duplicate samples (Fig 1), in every case where they are taken.

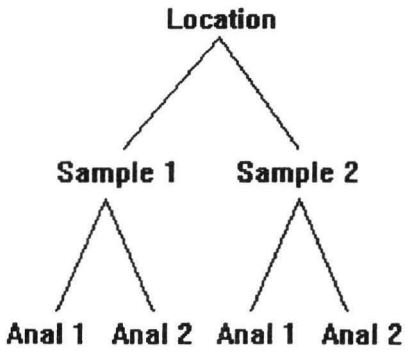

Fig 1. Balanced sampling design for the estimation of measurement uncertainty by Method 1.

This method requires a practical minimum of eight of the samples to be duplicated, which leads to 32 chemical analyses. The three components of the variability are separated using robust analysis of variance[13]. Two of the components can be classed as uncertainty, and these are the sampling and the analytical variance (s^2_{samp} and s^2_{anal}). The third component is the between-location variance due to real variation of the contaminant. In the case of spatial variability this has been called the geochemical variance ($s^2_{geochem}$). The sampling uncertainty, or within-location variance, will be partially due to small scale compositional variation within the location, but represents the uncertainty in all of the samples that could be taken from that 'location' as specified, with that sampling protocol. All three variance can be summed to give the total variance of the survey, expressed by:-

$$s^2_{total} = s^2_{geochem} + s^2_{samp} + s^2_{anal}$$

The measurement uncertainty (u) can be estimated, using this 'bottom up' approach, from the combination of the sampling and analytical variance, giving the measurement variance as:-

$$u = s_{meas} = \sqrt{(s^2_{samp} + s^2_{anal})}$$

To express the expanded uncertainty (U), with a coverage factor (k) of two (for 95% confidence) this gives:-

$$U = ku = 2\, s_{meas}$$

As relative uncertainty, this becomes:-

$$U\% = 200\, s_{meas} / \bar{x} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

A step-by-step explanation of the calculations of uncertainty using this method has been given elsewhere[14].

Sampling Design	Sites Duplicated	Mean Pb Robust $\mu g\ g^{-1}$	s_{total} Robust $\mu g\ g^{-1}$	s_{meas} Robust $\mu g\ g^{-1}$	U $= 2s_{meas}$	U% $=200s_{meas}/\bar{x}$
Regular Grid Single Sample	7	7516	8185	1871	3742	49.8%
Regular Grid Comp.Sample	9	6093	5600	940.5	1881	30.9%

Table 1. Estimation of measurement uncertainty from application of single sampler/ single protocol on Derbyshire site. Uncertainty reduced from 49.8% to 30.9 % by use of composite samples, as predicted theoretically.

When this method was applied to a spatial survey of lead at a site in Derbyshire, UK [1], using a regular grid of single samples (Table 1), the expanded uncertainty ($1871 \mu g\ g^{-1}$) is 49.8% (U%) for single measurements made at the estimated mean concentration of this site ($7516\ \mu g\ g^{-1}$). However, when five-fold composite samples where taken instead, the uncertainty drops to only 30.9% of the mean. This reduction in variance is statistically significant at the 95% confidence level, using the F test. This finding quantifies the theoretical prediction that taking composite samples should reduce measurement uncertainty. For example, Gy's equation predicts that the variance due to random sub-sampling should be inversely proportional to the mass of the sample [11]. Taking a five-fold composite would therefore be expected to reduce the uncertainty by a factor of the square root of five (2.24), if this were its only cause. The reduction in uncertainty in this example is by a factor of 1.6, which is smaller than this prediction and suggests that other factors may be involved. Whether such a reduction in uncertainty is necessary, will depend on whether the original measurements were fit-for-purpose, as will be discussed below.

The analytical bias (B_a, expressed as %) can be added to this estimate of the uncertainty, if it is known. For a measured concentration 'c', the upper limit of the range encompassing the true value of concentration can then be expressed by:-

$$c + U = c\ (1 + U\%/100 - B_a/100)$$

and the lower limit by:-

$$c - U = c\ (1 - U\%/100 - B_a/100)$$

For the example from Derbyshire, the analytical bias was determined to be –3% by the analysis of a range of suitable reference materials[1]. In this case, for a concentration at the mean of the single sample grid ($c = 7516 \mu g\ g^{-1}$, U% =49.8%, B_a = -3.0%), the upper limit of uncertainty is therefore given by:-

$$c + U = 7516\ (1 + 49.8/100 + 3/100) = 11484\ \mu g\ g^{-1}$$

The lower limit of uncertainty is given by:-

$$c - U = 7516\ (1 - 49.8/100 + 3/100) = 3999\ \mu g\ g^{-1}$$

These equations can be refined if either the bias or the precision varies as a function of concentration[15]. The main problem with this method is that it does not allow for bias originating from the sampling process. This may be caused by the variability between different sampling protocols designed to fulfil the same objective. Alternatively the sampling bias may arise between different samplers applying the same protocol. It has been suggested that the sampling bias of a particular protocol or sampler can be estimated by its application to a reference sampling target (RST) in addition to Method 1, discussed below.

The second procedure (Method 2) requires that one sampler applies a number of different sampling protocols, that have been selected to fulfil the same objective. The variation in the estimates of the specified parameter is used to estimate the measurement uncertainty. This parameter could either be the site mean or the concentration at particular sampling locations. In an application of Method 2 to the Derbyshire site [1], the determination of the mean concentration value gave a slightly increased estimate of uncertainty, compared with that from Method 1, which may be due to a contribution from the different biases from each protocol.

The third and forth methods require the use of a number of different sampling personnel (ideally 8 or more). The samplers use either the same protocol, applied twice (Methods 3) or different protocols that have been selected as being appropriate by each sampler for a common objective (Method 4). These methods detect the extra uncertainty caused by the personal bias introduced by each sampler (Methods 3), or that bias when combined with that introduced by each particular protocol (Method 4). It is important in designing such sampling trials, to maintain the independence between the samplers. Each sampler must leave no evidence of where they have sampled, and not communicate with other samplers prior to sampling. To give the best estimate of the uncertainty of the whole measurement process, each participant should also perform their own sample preparation and chemical analysis, either by one agreed method (Method 3) or by whatever method is considered appropriate by the participant (Method 4). If the objective is the estimation of the uncertainty originating solely from the field sampling process, then all of the samples can be prepared and analysed in one laboratory, under repeatability conditions (e.g. randomized within one analytical batch). High levels of uncertainty were found for the determination of the mean lead concentration at the Derbyshire site, both by Method 3 (55%) and by Method 4 (46%)[1].

Although an essentially 'top down' approach these two methods can also be adapted to give 'bottom up' information on the sources of the uncertainty. The duplication of the common protocol by each participant in Method 3, allows the estimation within-sampler variance. This is calculated from the reported concentration values using ANOVA as described for Method 1. It is debatable whether classical or robust ANOVA is preferable in this case[14]. This variance can be compared with the other sources of uncertainty, such as the between-sampler variance. In one contaminated land study, the similarity between these two sources suggested that site heterogeneity was the dominant cause of uncertainty rather than bias between samplers[8]. Replication of the chemical analysis on a proportion of the samples allows the estimation of the analytical precision, and its contribution to the uncertainty. When participants analyse their own samples, it is useful to include the analysis of a common reference material, that has been selected to closely

match the composition of the samples. This allows the estimation of the analytical bias for each participant and the contribution that this makes to the overall uncertainty.

In addition to the estimation of uncertainty, the findings from Method 3 can be used as a Collaborative Trial in Sampling (CTS) for the validation of a particular sampling protocol for a particular site[12]. Method 4 also constitutes a Sampling Proficiency Test (SPT), which can be used to assess the performance of sampling personnel at a particular site[3]. Future SPT designs could usefully include the reporting of estimates of uncertainty by each participant. This would provide interesting comparisons between the estimates of uncertainty made by the different methods, and by different participants. Unlike such 'top-down' methods for the estimation of analytical uncertainty, such estimates for sampling uncertainty are site specific. Further work on sites of a similar type may show however, that certain protocols or participants generally perform better than others.

INDEPENDANT ESTIMATION OF SAMPLING BIAS

Sampling bias is an important component of the uncertainty that can be estimated by these methods using inter-organisational sampling trials, However, such trials are relatively expensive, but a less expensive method for estimating sampling bias is possible by the creation of a reference sampling target (RST). An RST is the sampling equivalent of a reference material (RM) used for the estimation of analytical bias [9]. A candidate RST has been prepared already by running inter-organisational sampling trials on the contaminated site in Derbyshire, with selected participants using a wide range of sampling protocols and different analytical methods. An accepted value for the contaminant concentration, and its uncertainty, have been established from a consensus of those submitted by all of the participants. The sampling bias for a new sampler or protocol can be estimated by comparison with the accepted value, in an analogous way to use of RMs for the estimation of analytical bias. A synthetic RST has also be prepared at Ascot, UK, in which a known concentration of contaminant was added to a sampling target. In this case, the bias of participant's measurements can be estimated by comparison with the known value, rather than against a consensus value.

There are limitations to the use of RSTs for the estimation of sampling bias. Some degree of heterogeneity in the RST is inevitable and realistic, but does limit the size of the sampling bias that can be detected [8]. For RMs the relevance of the estimated analytical bias to the samples themselves depends on having a close match between the composition of the reference material and the samples. Similarly, the use of an RST to estimate sampling bias is strictly site-specific and the applicability of the findings to another sampling target depends on the degree of similarity between the characteristics of the RST and the new target.

Given these new independent methods for the estimation of sampling bias, is should be possible to provide a modification to Method 1 by which a single sampler can make a more realistic estimate of measurement uncertainty as part of a routine contaminated land investigation.

UNCERTAINTY AS TOOL FOR EVALUATING FITNESS-FOR-PURPOSE

There is an increasing recognition that the main criterion that should be used to judge a site investigation of contaminated land is the quality of the conclusions that can be made,

rather than the analytical quality of the measurements [16]. This is equivalent to making the criterion that the measurements (including the sampling) should be 'fit-for-purpose' (FFP), a well accepted concept in quality assurance. This implies that no single sampling protocol would be appropriate for all site investigations; it should be appropriate for the particular purpose at the particular site. What is required therefore is a criterion by which fitness-for-purpose can be judged, for whatever protocol is used. For geochemical investigations in general, one such criteria has been suggested, namely that the measurement variance (s^2_{meas}) should not exceed 20% of the total variance (s^2_{total}) of the concentration values for any analyte [17]. When this proportion is exceeded the reliability of the differences between the levels of contaminant concentration between different locations on a site becomes progressively degraded. It was also been suggested that the analytical variance should not contribute more than 20% to the total measurement variance, if it is not to contribute significantly. In the example described above for Method 1 from Derbyshire [8], the taking of composite samples did reduce the measurement uncertainty from 49.8% to 30.9%. This reduction was not justified however, as the measurement variance using the non-composite samples only contributed 5.2% to the total variance, which was already less than the FFP value of 20% of the total variance.

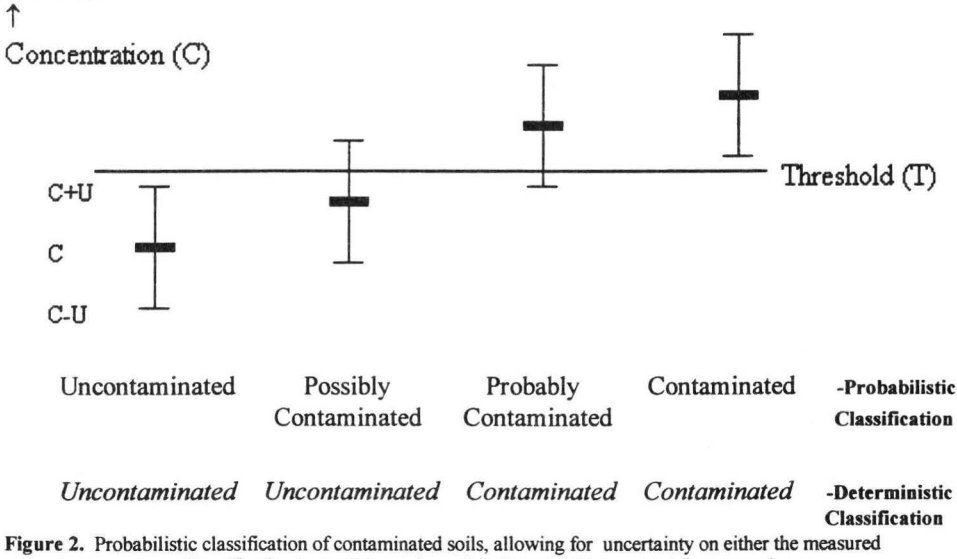

Figure 2. Probabilistic classification of contaminated soils, allowing for uncertainty on either the measured concentration values. Classification by traditional deterministic method is provided for comparison.

A second FFP criterion can be related to the effect of uncertainty on the classification of contaminated land. Once estimates of uncertainty (U) are known, it is possible to use a probabilistic, rather than the traditional deterministic classification [1]. For example, when a particular location has an estimated concentration of a contaminant (C) that is below some regulatory threshold (T), it would traditionally be classified as 'uncontaminated' (Figure 2). If however the upper limit if the uncertainty interval (C+U) is greater that T, then this location can be classified as 'possibly contaminated' [1]. There is a stated level of probability (0.025 to 0.500) that this location might be contaminated over the threshold value. Four classes of contamination can be recognized based on the different probability of contamination (Table 2). For any investigation, therefore, there will be a larger number of sites that will be classified as 'possibly contaminated' that

would have been classified as 'contaminated' under a deterministic scheme. It is possible to select a suitable level of probability that reflects the particular financial consequences of mis-classification at a particular site.

Classification	**Concentration Range** *with uncertainty on C*	**Probability of C > T** i.e. C being over threshold
Uncontaminated	C + U < T	<0.025
Possibly contaminated	C < T < C + U	0.025 - 0.500
Probably contaminated	C - U < T < C	0.500 - 0.975
Contaminated	T < C - U	>0.975

Table 2. Probabilistic classification of soils with measured concentration (C) and uncertainty (U), based on the probability that the contaminant concentration is greater than a particular threshold value (T). Uncertainty values are stated for 95% confidence interval, but could be recalculated for what ever confidence interval is considered appropriate

The advantage of the probabilistic approach is that there is increased confidence that land will not be misclassified, and therefore a reduction in the chances of litigation. The disadvantage of the probabilistic approach is that more land must be considered as possibly contaminated, and therefore there is a potential increased cost of treatment. If however the uncertainty of the measurements is decreased then the proportion of the land classified as 'possibly contaminated' decreases, and expense is saved. There is a balance to be found therefore, between the expenditure on improved measurements to reduce uncertainty, and the cost of treatment of possibly contaminated material. It has been suggested that an economic loss function is used to establish FFP in such cases [18]. This will allow the optimum expenditure to be apportioned between the cost of measurement and the cost of action on the suspect material. It can also be applied to balance between the costs of the sampling and that of analysis within the measurement process, on the basis of minimizing both the uncertainty and the cost.

CONCLUSIONS

1. The estimation of measurement uncertainty is a new practical tool for improving the reliability of contaminated land classification.
2. The four proposed methods range in complexity and expense, and give increasingly reliable estimates of uncertainty, that include components from sampling bias. They also identify and quantify the different sources of uncertainty
3. High levels of uncertainty (>50%) have been found in field trials. Sampling procedures were shown to be the dominant source of the measurement uncertainty, rather than the chemical analysis.
4. Further sampling trials are required to establish the general levels of uncertainty at a wide range of sites, and for a range of objectives. Estimation of measurement uncertainty for the spatial delineation of 'hot spots' of contamination is an objective of current study.
5. The inter-organisational sampling trials also provide a tool for assessing and accrediting sampling personnel, which should also lead to an improvement in the quality of sampling.
6. The uncertainty can be used as a criterion to judge the fitness-for-purpose of a set of measurements for a site. A simply applied criterion is the ratio of the measurement variance to the total variance for each contaminant across the site (<20%). A more

sophisticated criterion could be developed to balance the cost of reducing the uncertainty in the measurements against the savings in treatment of misclassified land.
7. This approach amounts to a change in emphasis for site investigation away from the pursuit of the ideal sampling protocol, to the pursuit of the most appropriate protocol, judged by an acceptable level of measurement uncertainty.

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ON DIFFUSIVE MASS-TRANSFER LIMITATIONS IN RELATION TO REMEDIATION OF POLLUTED GROUNDWATER SYSTEMS

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Key words: in-situ groundwater remediation, mass transport, diffusion, immobile zones, pumping

SUMMARY

Limited diffusive mass transfer is one cause for stagnant groundwater remediations. We characterise the diffusive mass transfer process as a three stage cyclic process of mass transfer into and out of stagnant or immobile zones. The first stage is the contamination stage, where net inward diffusive mass transfer happens and the last stage is the remediation stage where the opposite happens. An intermittent stage may happen when the immobile zone has reached equilibrium with the mobile zone. Using an analytical solution for diffusive mass transfer into and out of an immobile zone, we show that decades may be involved to reach this stage for natural systems. If this stage does not get reached, continuous inward diffusion happens during the remediation stage. Then, the remediation period required lasts much longer than the contamination period available. Numerical simulation for a simplified two-layer mobile/immobile system further shows that excessive pumping rates do not speed up remediation, since the rate-limiting process is not significantly affected by this. Intermittent pumping or continuous pumping at low rates is equally effective from remediation point of view. Other criteria are then decisive whether continuous pumping or intermittent pumping is most interesting.

Contaminated Soil '98, Thomas Telford, London, 1998, 231–240

INTRODUCTION

Prolonged tailing is often encountered during in-situ remediation of groundwater contamination plumes. One cause for prolonged tailing is the limited diffusive mass flux of the contaminant from less permeable zones (stagnant or immobile zones) to more permeable zones, where advective groundwater flow dominates (mobile zones). Many remediation stategies therefore turn out to be overdimensionized. Optimization of remediation stategies is noteworthy for reasons of environmental and economic benefit.

Investigations on optimization of pump-and-treat techniques have been performed in the past few years. The investigations focus on two aspects: 1. the effect of aquifer heterogeneity (Rabideau & Miller, 1994; Berglund & Cvetkovic, 1995) and 2. the efficiency of intermittent pumping versus continuous pumping (Harvey et al., 1994). The investigations usually focus on groundwater concentrations within the mobile, advection dominated zone. We studied the diffusive mass transfer process within the stagnant, immobile zone and the related transverse mass transfer process between the mobile and the immobile zone, i.e., we have characterised the cyclic diffusive mass transfer process into and out of immobile zones for pulse-type cases. The specific objectives of this study are as follows. First, we characterise the mass-transfer process into and out of stagnant layers within the context of aquifer remediation. Second, we examine the time periods that are involved to fill stagnant zones in natural porous media, its implications for the associated time periods for remediation of these media and the related pumping strategy.

THEORY

Diffusive mass-transfer is described by Fick's second law:

$$\frac{\partial c}{\partial t} = D' \frac{\partial^2 c}{\partial x^2} \tag{1}$$

where c is aqueous concentration, t is time, D' is diffusion coefficient and x is distance. The diffusion coefficient is equal to the effective diffusion coefficient in a porous medium when conservative transport is involved, and it is equal to the apparant diffusion coefficient when linear retardation in a porous medium happens due to sorption. When appropriate initial and boundary conditions are used, analytical solutions can be obtained for cyclic diffusion into and out of a porous medium from those for continuous diffusion into a porous medium. The analytical solution is obtained from Carslaw & Jaeger (1959) or Crank (1975), using the principle of superposition, where diffusion happens into and out of a homogeneous layer for the case of a solute in contact with the exterior of the layer for a limited time (Griffioen, 1998):

$$c^*(x^*,t^*) = 1 - A(x^*,t^*), \quad 0<t^* \leq t_{in} \tag{2a}$$

$$c^*(x^*,t^*) = A(x^*,t^* - t_{in}) - A(x^*,t^*), \quad t^*>t_{in} \tag{2b}$$

with:

$$A(x^*,t^*) = \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}e^{-(2n+1)^2\pi^2 t^*/4}\cos\left(\frac{(2n+1)\pi x^*}{2}\right) \quad (2c)$$

and with the following initial and boundary conditions:

$$\frac{\partial c^*(0,t^*)}{\partial x^*} = 0 \quad (3a)$$

$$c^*(x^*,0) = 0 \quad (3b)$$

$$c^*(1,t^*) = 1 \quad 0<t^*\leq t_{in} \quad (3c)$$

$$c^*(1,t^*) = 0, \quad t^*>t_{in} \quad (3d)$$

where the following nondimensional parameters are defined:

$$c^* = c/c_{out} \quad (4a)$$

$$x^* = x/L \quad (4b)$$

$$t^* = D't/L^2 \quad (4c)$$

where c^* is relative concentration, c_{out} is the boundary concentration on the outside of the infinite layer, t^* is relative time, x^* is relative distance from the middle of the layer and L is half the thickness of the layer, and t_{in} is the period during which the exterior of the layer is in contact with a fluid containing a solute of c^* is 1.

MODELLING APPROACH

The above presented analytical solution cannot be used when no discrete concentration changes occur at the exterior of the stagnant zone. This is more likely in natural systems, where aquifer remediation using e.g. pump-and-treat is applied. We used the finite difference transport model MT3D (Zheng, 1992) to study mass transfer into and out of a stagnant clayey layer that is in contact with a permeable sand layer.

Contamination histories were simulated using a sandy layer of 10.0 meters long, 1.0 meter width and 2.0 meters thick with a hydraulic conductivity of 5.0 m/day. Adjacent to this layer is an impermeable layer of similar geometry, but with a hydraulic conductivity of $10^{-5.0}$ m/d. The discrepancy of the permeability between mobile and immobile zones was chosen this large, to assure that exchange of contaminant between the zones is only due to diffusion.

Two contamination cases were considered: a retardation factor of 1.9 and one of 9.9, respectively. This corresponds to transport of toluene and that of naphthalene with an

organic matter content of 0.16%, porosity of 0.3 and specific density of 1860 kg/m^3. The contaminant source was modelled as cells with a constant concentration at the upstream side of the model. 'Natural' groundwater flow along the source cells caused the contamination to enter the sandy layer. The pore water velocity was 15 m/yr. The period of contamination lasted 20 years. This resulted in a situation where the stagnant zone is almost in full equilibrium for toluene, but not at all for naphthalene.

The performance of the numerical approach was evaluated by comparing results with an analytical solution of Duijn and Van der Zee (1986) for solute transport in a horizontally layered two layer system. The analytical solution describes the average concentration in the more permeable zone, accounting for transversal dispersion between the two layers and neglecting longitudinal dispersion. The concentration difference between the two approaches is at most 5 percent for naphthalene and less for toluene. This is attributed to numerical dispersion of the initial sharp concentration gradient between the permeable and the stagnant zone. The numerical approach is considered to be satisfactory at the used scale of discretisation (thickness of model cell 20 cm.).

In situ remediation by pump-and-treat was simulated by inflicting a hundred-fold increase of the groundwater velocity and reversing the direction of the flow. It should be noted that the simulated velocity field during remediation was uniform and not radial as one would expect in case of flow to a single well. Therefore, the results of this study can be applied to areas not too near to wells, where flow velocity changes much along a short distance. The period of remediation lasted 20 years as well. Two remediation strategies were compared with respect to efficiency: continuous pump-and-treat during 20 years and pulsed pump-and-treat during 20 years.

RESULTS

Figure 1 presents, for sake of convenience, the trend in concentration during continuous net inward mass transfer. The figure shows that the concentration is still 0 at $x^* = 0$ for $t^* = 0.05$ and that for larger t^* the solute diffuses up to the middle of the layer. The

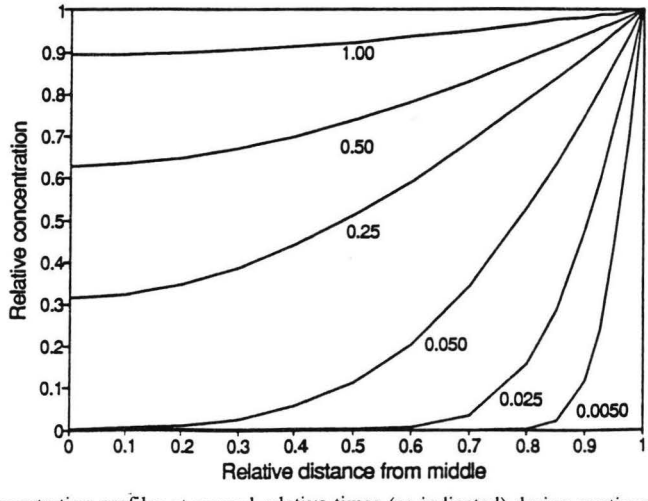


Figure 1. Concentration profiles at several relative times (as indicated) during continuous net inward mass transfer.

relative concentration in the middle of the layer is 0.9 for $t^* = 1.0$. The layer can in practice be considered as in near-equilibrium with the permeable zone for t_{in} is larger than 1.0.The period during which no further contamination happens will be called the equilibrium period. The first period where net inward transport of contaminant happens, i.e., t_{in} is smaller than 1.0, will be called the filling period.

The time span required for stagnant layers to fill can be evaluated in a general way from literature data on diffusion coefficients, using eq. [4c]. The upper limit for diffusion of aqueous solutes is approx. 1.0E-09 m^2/s. Experimentally determined values for the effective diffusion coefficients of solutes range from 10^{-9} to 10^{-14} m^2/s; here, the empirical studies considered two different types of solids: aggregates comprised of individual grains (e.g., Rowe et al., 1988; Myrand et al., 1992) and loose grains having diameters of approx. 0.01 to 1 mm (Wu & Gschwend, 1986; Grathwohl & Reinhard, 1993). The apparent diffusion coefficient can thus be as low as 10^{-16} m^2/s when a retardation factor of 100 is encountered. This retardation factor can be expected, e.g. for the adsorption of trichloroethylene in a peaty solid matrix containing 10 % organic carbon.

Note that diffusion lengths equal to the radius of spherical media have always been assumed while fitting the mathematical diffusion concept to the experimental measurements. This seems realistic for aggregates, but may be erroneous for individual grains: diffusion lengths equal to the radius will mean voids up to the centre of the porous medium and this raises doubt about whether such a medium is still a firm grain or should be considered to be an aggregate. This is even more pertinent when one remembers that fitting is often based on measurements of the aqueous concentration of the bulk solution.

Figure 2 shows the characteristic time required to fill the stagnant layer for three relative time steps and two values of the diffusion coefficient (the coefficient may be apparent for reactive transport, or effective for conservative transport). Clearly, time spans in the order of years can be expected for layer thicknesses in the order of

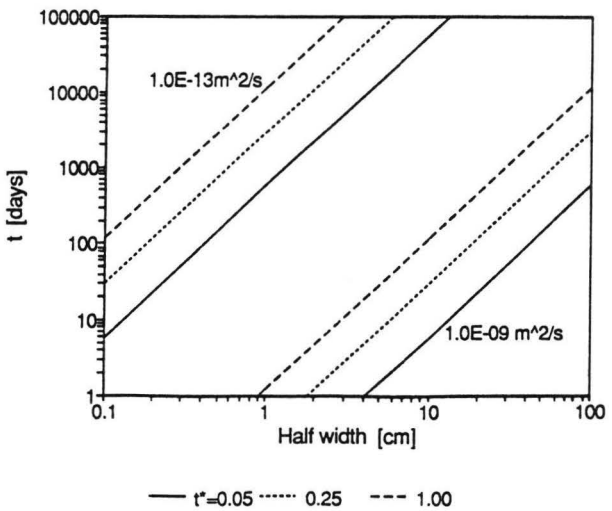


Figure 2. Relationship between real time and half width of stagnant layer for filling up to three relative time intervals (t^* is 0.05, 0.25 and 1.0) and two diffusion coefficients (1.0E-9 and 1.0E-13 m^2/s; see values indicated).

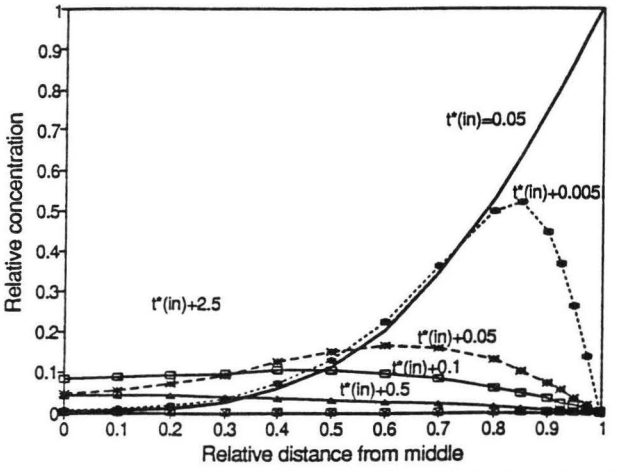


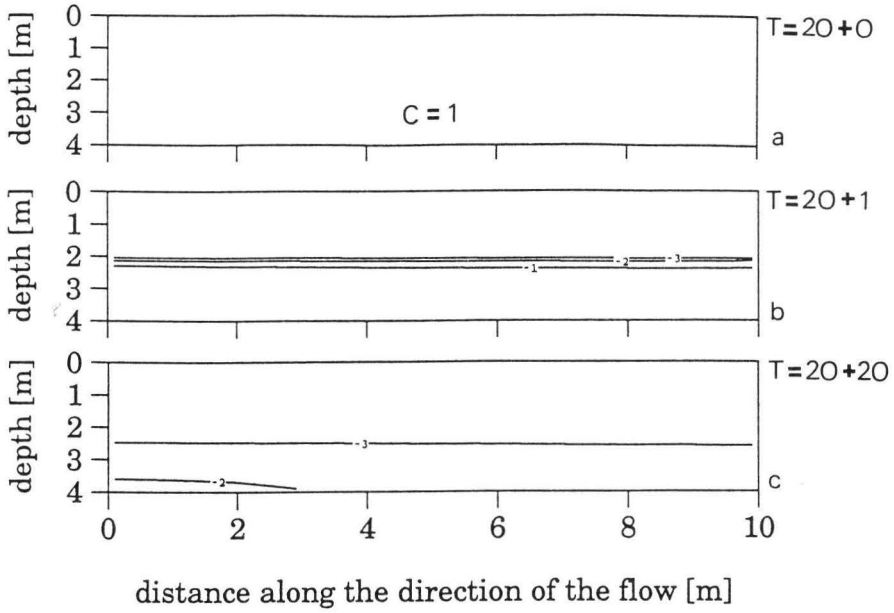
Figure 3. Concentration profiles in a stagnant layer at various relative times (as indicated) during the remediation period when the filling period t_{in} was 0.05.

centimetres to decimeters. For slowly diffusing compounds such as PAH's, (tens of)years are even involved to reach equilibrium between the mobile and the stagnant zones when the latter are less than a centimeter. The usual age of contamination cases is in the order of tens of years; gas works can be as old as one century. This illustrates that filling of stagnant zones can be incomplete for actual contamination cases.

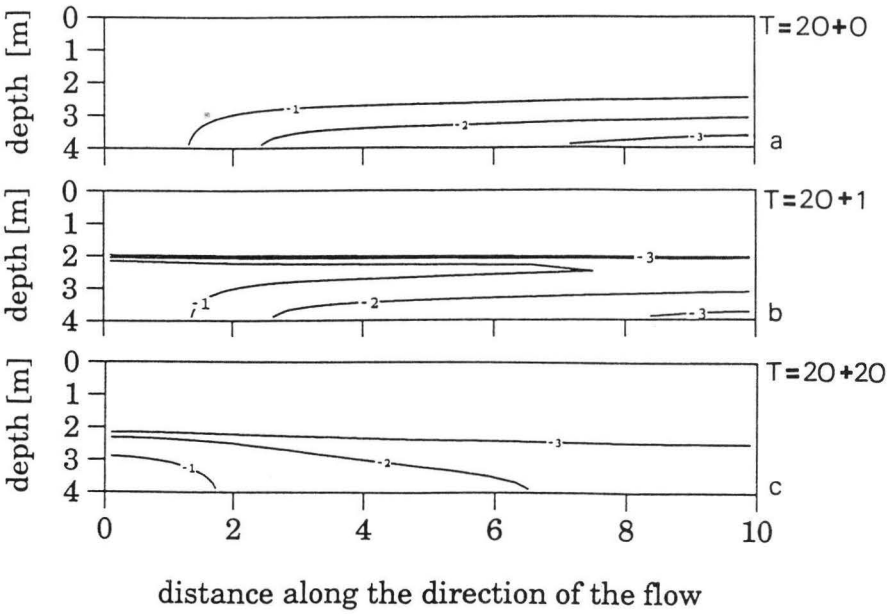
Interesting phenomena can be noticed when incomplete filling has happened (Griffioen, 1998). Figure 3 shows as an example the development of the concentration profiles within a stagnant layer during the remediation stage when t_{in} was 0.05. Two major observations can be made. First, diffusion into the stagnant layer happens during the first part of the remediation stage, because of the steep concentration gradient within the stagnant zone. The contaminant thus moves into two opposite directions during remediation in case of incomplete filling. Second, the relative time period required for the desorptive stage, i.e., for remediation, is long compared to that for the adsorptive stage, i.e., for contamination. The remediation period is easily more than ten times the contamination period, when incomplete filling has happened and the relative concentration has to decrease to 0.01.

For a contamination period, t_{in}, of 1.0, the relative concentration is less than 0.1 at any location in the layer after a relative remediation period equal to 1.0 (not shown here); the relative concentration is less than 0.01 for a relative remediation period that equals 2.0. This illustrates that remediation periods will at least be as long as the contamination period, if diffusive mass transfer controls mass transfer and low concentrations have to be attained. Prolonged periods are thus required for remediation of stagnant zones when diffusive mass transport happens within these zones. Natural subsurface systems will behave somewhat differently, because the concentration gradients at the edge of stagnant zones are not as sharp as assumed in the analytical approximation presented.

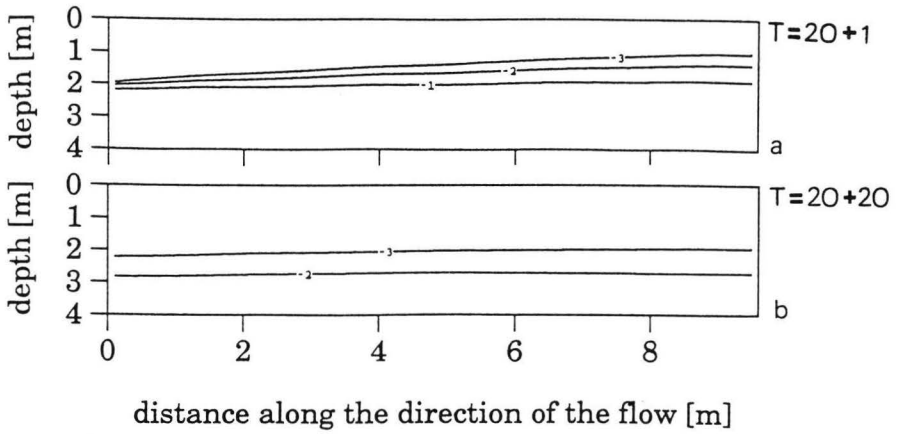
Figures 4a and 5a show concentration patterns of toluene and naphthalene as logarithmic values after a 20 year period of contamination for the contamination histories described. Both toluene and naphthalene concentration are equal to the input concentration in the entire permeable zone. The toluene concentration in the stagnant zone resembles the



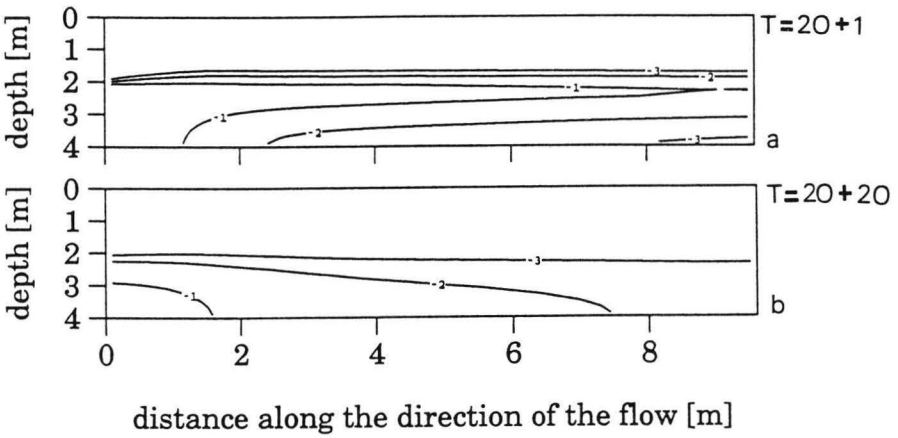
Figures 4. Plots of log value of the toluene concentration in a two layer medium (with 0-2 m permeable zone and 2-4 m stagnant zone) from a contamination period of 20 years on in case of continuous pumping.



Figures 5. Plots of the log value of the naphthalene concentration in a two layer medium (with 0-2 m permeable zone and 2-4 m stagnant zone) from a contamination period of 20 years on in case of continuous pumping.



Figures 6. Concentration plots of naphthalene in a two layer medium from a contamination period of 20 years on in case of intermittent pumping.



Figures 7. Concentration plots of naphthalene in a two layer medium from a contamination period of 20 years on in case of intermittent pumping.

concentration of the permeable zone and the equilibrium period has thus been reached for the stagnant zone. The naphthalene concentration in the lower reaches of the stagnant zone is only a few percent of the naphthalene concentration in the permeable zone. The stagnant zone is still getting contaminated after 20 years; the system is still in the filling period for the more strongly sorbing contaminant. The longer time span needed can be attributed to a combination of two effects: 1. less adsorbing contaminants like toluene move faster through the sandy layer, so diffusion into the stagnant zone starts earlier at a fixed position, and 2. the apparent diffusion coefficient of weakly adsorbing compounds as toluene is much larger than that of a strongly one as naphthalene.

The characteristic time to fill stagnant zones explains the different progress of the remediation of the toluene and naphthalene contaminated system (cf. Figures 4 and 5). Within a few days, both toluene and naphthalene are removed from the permeable zone by advective flow and a steep concentration gradient between the stagnant and the permeable zone is established. The stagnant zone is slowly remediated by a diffusive

mass flux out of the stagnant into the permeable zone. Interesting is that the non-equilibrium state of the naphthalene contaminated stagnant zone causes an inward diffusive mass flux, which is in accordance with analytical results (Figure 5b): the stagnant zone is being remediated close to the mobile zone as well as getting polluted more inward at the same time. After 20 years, the progress of the remediation of the toluene contamination is much larger than that of the naphthalene contamination, although much more toluene had to be removed at the start of the remediation period (cf. Figures 4c and 5c). This needs to be attributed to the larger apparent diffusion coefficient for toluene compared to that for naphthalene.

A comparison was made between the efficiency of continuous and pulsed pump-and-treat. Pulsed pump-and-treat is believed to be more efficient in terms of volumes of pumped groundwater for the remediation of two-zone porous media, where mass transfer between stagnant and permeable zones is rate limited. Pumping is only required to remove mass from the permeable zone and should be stopped when mass removal gets limited by diffusion of contaminant out of the stagnant zone. After pumping has ceased, concentrations in the permeable zone will rise again, and spreading of the contaminant in the permeable zone may occur due to natural groundwater flow. An unacceptable extent of spreading is the sign to resume pumping. The environmental benefit of this strategy is that less groundwater is pumped while the same amount of mass removed.

Pulsed pump-and-treat was engineered as 20 cycles of one year in which the permeable zone was flushed R times per cycle (where R is the retardation factor for toluene or naphthalene, respectively). For this particular case, one cycle consisted of 4.6 pumping days for toluene and 24 pumping days for naphthalene. Natural groundwater flow happens for the rest of the year. The total volume of extracted groundwater is 240 m^3 for toluene and 1300 m^3 for naphthalene compared to a volume of 19700 m^3 which is extracted during continuous pump-and-treat at a pore water velocity of 1500 m/day. Comparison of Figures 5c and 7b reveals that pulsed pumping results in similar naphthalene concentrations in the stagnant zone as in the case of continuous pumping, but 7% of the groundwater volume is extracted compared to continuous pump-and-treat.

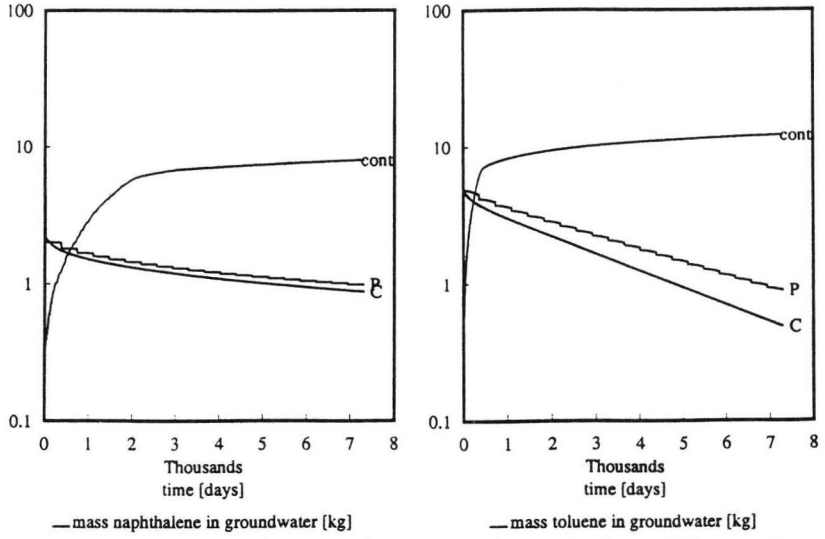


Figure 8. Amount of dissolved mass present during 20 years of contamination and 20 years of remediation for naphthalene (left) and toluene (right).

Pulsed pumping of toluene is somewhat less efficient regarding the resulting concentration in the stagnant zone (cf. Figures 4c and 6b). However, the volume of extracted groundwater is only 1% of that in the case of continuous pumping.

The amount of mass of contamination present was calculated to compare pulsed and continuous pumping: Figure 8 shows that continuous pumping is somewhat more efficient in removing mass out of stagnant zones, although the differences are small. Other criteria are then decisive whether continuous or pulsed pumping is most interesting. Pulsed pumping can be a cheaper alternative if sharing of a treatment installation between several contaminated sites is possible. A mobile treatment unit could serve several closely situated sites, if the duration of the interval between pumping is large enough compared to the number of sites. In our case, almost 50 toluene contaminated sites or 14 naphthalene contaminated sites could be treated on a yearly basis with just one ex-situ treatment unit. One should avoid that the contaminant gets transported out of the reach of the capture zone of the withdrawal pump by natural groundwater flow. The duration of the interval between pumping might have to be more reduced in order to prevent this unwanted spreading. The presence of several contaminants may complicate optimization of remediation cycles.

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SOIL EXTRACTION METHODS FOR THE ASSESSMENT OF THE ECOTOXICOLOGICAL RISK OF SOILS

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Key words: mobility, soil elution/extraction methods, toxicity potential, PAHs, trinitrotoluene, hydrocarbons

SUMMARY
A combination of chemical and biological analytical methods has been proofed as suitable for an estimation of a possible groundwater contamination by contaminated and remediated soils. A broad set of methods is proposed for the preparation of soil eluates. A comparison of the concentrations of contaminants in soil eluates shows that a soil/water ratio of 1/2 is most practicable. In these eluates the concentration of the pollutants in all samples range slightly above the concentration in soil saturation extracts. For preparing soil eluates for analytical determinations or ecotoxicity tests appropriate clean up steps are very important. A combination of centrifugation and filtration by glass fibre microfilters or a combination of two filter types is recommended.

KURZFASSUNG
Für die Abschätzung des Grundwassergefährdungspotentials kontaminierter und gereinigter Böden hat sich eine Kombination aus chemischer und biologischer Analytik zur Erfassung mobiler Schadstoffe und deren Toxizitätspotential als geeignet herausgestellt. Für die Herstellung von Bodeneluaten liegt ein breiter Satz an verschiedenen Methoden vor. Der Vergleich der Schadstoffkonzentrationen in den Eluaten bei verschiedenen Boden/Wasser-Verhältnissen belegt, daß das vorgeschlagene Boden/ Wasser-Verhältnis 1:2 praktikabel ist. Für die Aufarbeitung (clean up) der Proben hat sich eine Kombination aus Zentrifugation und Glasfasermikrofilter bewährt..

RÉSUMÉ
Pour estimer le danger que les sols pollués ainsi que les sols purifiés présentent pour les eaux souterraines une combinaison d'analyses chimiques et biologiques a prouvé d'être convenable afin de déterminer les polluants mobiles et leur potentiel toxique. Pour la préparation des extraits du sol un grand spectre de méthodes différentes existe. La comparaison des concentrations des substances nocives dans les extraits du sol pour des proportions sol/eau différentes prouve qu'une proportion sol/eau de 1:2 est practicable. En ce qui concerne la préparation des échantillons (clean up) une combinaison de centrifugation et des microfiltres à fibre de verre est recommandée.

Contaminated Soil '98, Thomas Telford, London, 1998, 241–250

Introduction

Soil extraction methods and soil elution procedures, respectively, are applied for different purposes. Accordingly, a large set of elution/extraction methods is described in the literature, and a systematization seems to be difficult. Figure 1 is the attempt of presenting an overview over available elution and extraction methods by classification according to application objectives.

Soil eluates are used to quantify the mobile and available portions of contaminants in soils and soil substrates. The identification and characterisation of polluted sites is mainly based on the total content of pollutants. Also the trigger values for soil remediation are given by chemical analysis of the total content of the main pollutants. However, for routine analysis the number of pollutants has to be restricted to the expected ones due to feasibility and for cost reducing reasons. For groundwater protection the determination of mobile portions is of relevance. The first step of a substance related assessment is a chemical analysis of soil eluates This analysis should be enlarged by a combination of chemical and ecotoxicological analyses to ensure that the toxicity potential of the soil extract is indicated. For this purpose test batteries comprising various tests with organisms of different sensitivity and, if necessary, different endpoints, should be applied. The test organisms need not be representative for soils or soil pore water, since the tests do not indicate potential hazard for the habitat soil, but focus on a most significant analytical determination of toxicity potentials.

When soil extracts are applied to obtain information about the bioavailability of soil contaminants for the compartment soil either valid correlations for the transfer paths soil → organisms, as e.g. the transfer path soil → crop should be available, or tests with soil relevant organisms should be conducted. In both cases it is a prerequisite that the main route of exposure for the investigated contaminants as well as for the tested organisms is via the soil solution. Nevertheless, for an assessment of soil quality and the habitate function of soils, test with soils or soil substrates and relevant soil organisms should be performed.

Table 1 shows a selection of different elution methods to present important procedures of the broad spectrum. The presented procedures vary with respect to soil/water ratio, pH value, number of elution steps and elution period.

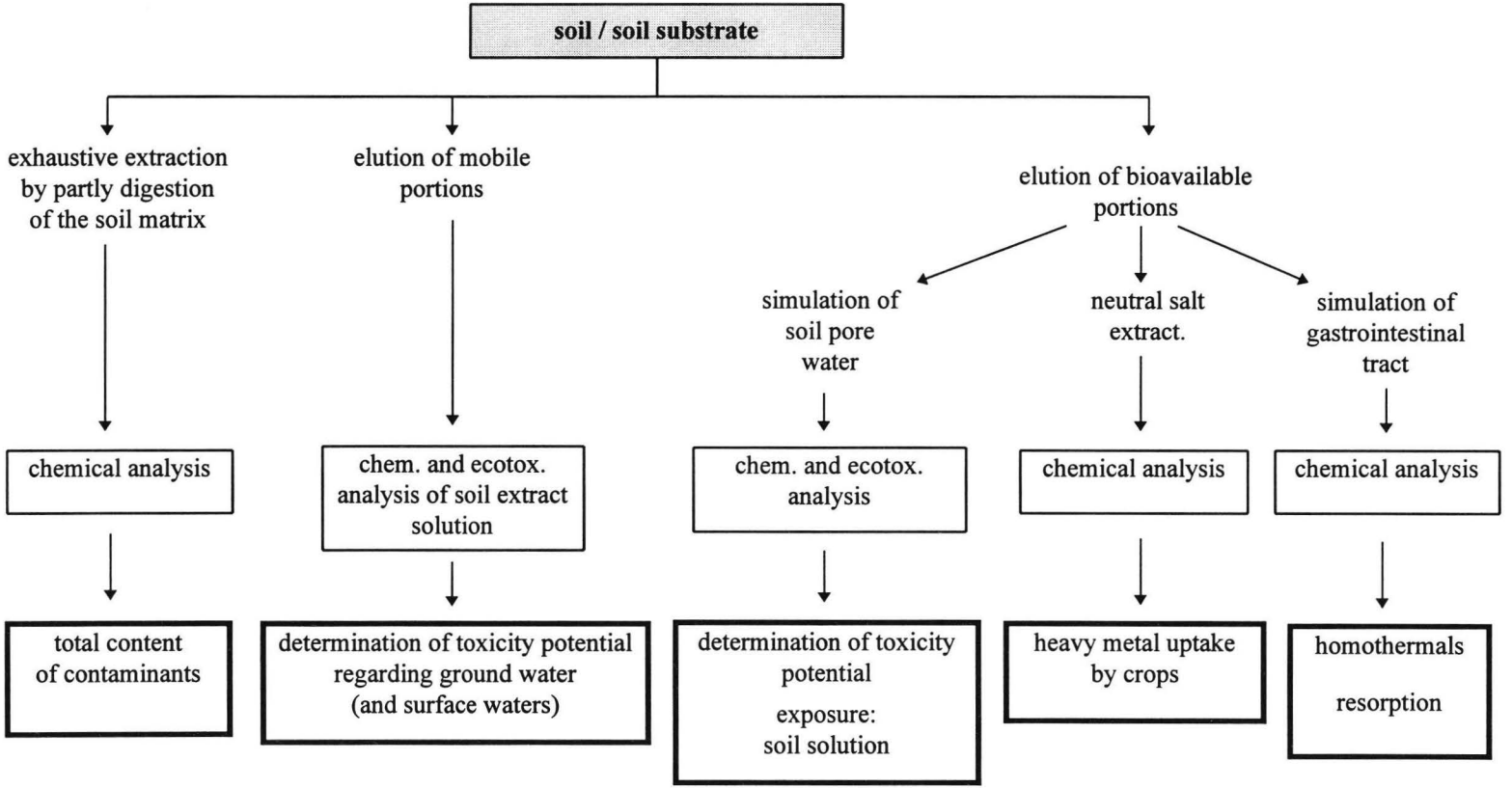

Figure 1.
Objectives for soil extraction/soil elution procedures

Table 1. Overview over elution procedures

Procedure	Solid/liquid ratio	pH value	Time	Extract
	ratio of liquids			
soil saturation extract	~ 1 : 0.6	-	24 h	1
S4 - procedure	1 : 10	-	24 h	1
pH - stat - procedure	1 : 10	4; 11	24 h	1
DECHEMA	1 : 2	-	24 h	1
DIN V 19730 (soil)	1 : 2.5 (NH_4NO_3)	-	2 h	1
Swiss eluate test	1 : 10	4.0 - 4.5	24 h	2
cascade test (NEN 7343)	shaking method 1 : 20	4,0	23 h	5 fract.
column test (NEN 7343)		4,0		7 fract.
column test DIN 19736 (draft)			5-15 pore vol. 2-7 days	-

according to Blankenhorn

Material and Methods

Within a joint project sponsored by the BMBF (federal ministry of research) a set of soils polluted by PAHs, hydrocarbons (oils) and nitroaromates were investigated. Table 2 givs an overview on the characteristics of those soil for which results are presented.

For elution different solutions were applied, water, 0.01 $CaCl_2$ and DOM solutions. The DOM was eluted from a compost. Different soil/water ratios were used in the range of 1/0.6 to 1/10 soil/solution). In addition the soil elution was repeated different times.

After shaking, the suspension was centrifuged either at 650 x g for 20 minutes or at 27.800 x g for 20 minutes. Thereafter the supernatant was filtrated either by glass fibre microfilters (0.7 µm) or by pressure filtration (cellulose nitrate membrane filters (0.45 µm); nylon membrane filters (0.45 µm)).

Table 2. Soil characterisation

Soil	pH	C_{org} [%]	PAH [mg/kg]	TNT [g/kg]
E-PAH	7.5	0.5	387.5	
Hallschlag 1	5.1	9.9		30.0
Hallschlag 2	4.9	25.7		20.2

Results

Comparison of soil elution methods

The influence of the selected methodology on the concentration of the contaminant in the eluate is demonstrated by figures 2 and 3 for the examples of a PAH and a TNT contaminated soil. Both examples clearly demonstrate that shaking of the samples results into higher concentrations than determined in the soil saturation extract (realistic worst case), which is due to thorough mixing of the sample and the resulting partly destruction of soil aggregates. Depending on the soil type the highest concentration is obtained for a soil/water ratio between 1/1 and 1/2. The amount of water which is needed to get a thoroughly mixed soil/water suspension depends on the soil properties. Increasing soil/water ratios result in decreasing substance concentrations in the eluate. The decrease of the concentration depends on the soil as well as on the physico-chemical properties of the pollutant and its concentration. Shaking should be sufficient to reach an equilibrium between solid soil phase and water phase (K_f- value).

Repeated soil elution procedures may be appropriate to elucidate, if the concentrations of the pollutants in soil elution may decrease rapidly or stay over a longer time. The comarison of six repeated elutions of a soil contaminated by PAH and a soil contaminated by nitroaromates show the expected results. Nitroaromates reveal in much higher concentrations in the eluate than PAHs. Correspondingly the concentrations decrease faster. Elutions by $CaCl_2$-solutions show slighly lower concentrations compared to water. This may be caused by a better separation of small soil particles. This assumption is confirmed by the observation that repeated elution with destilled water leads to a desalting of the soil resulting in a destabilisation of soil aggregates. This makes a separation by centrifugation at 650 x g impossible. DOM containing solution showed only a week solubilizing effect. This is caused by the fact that mainly fluoranthene is elution which not poorly soluble.

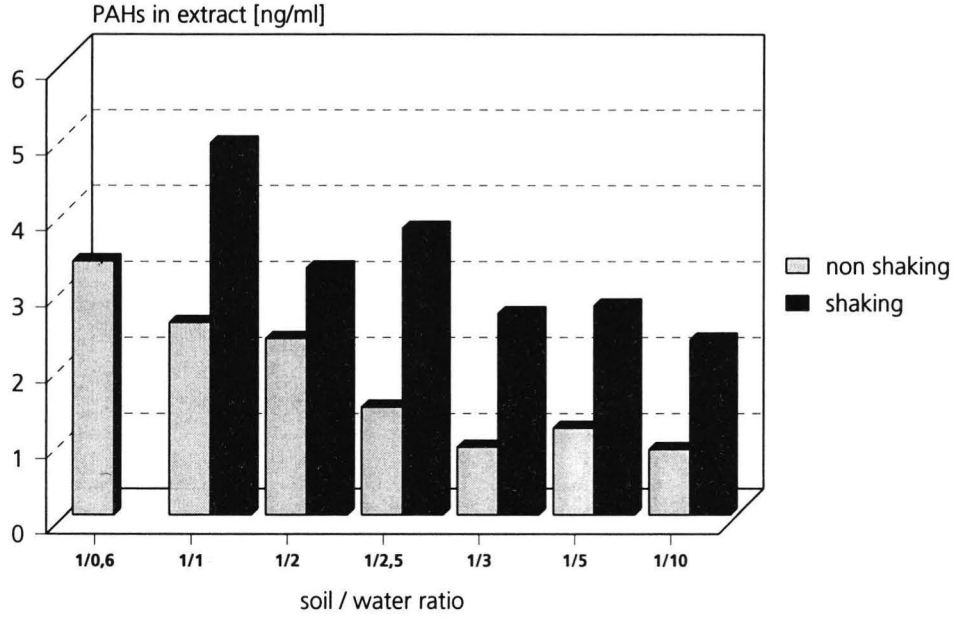

Figure 2.
Variation of soil/water ratio
soil contaminated by PAHs

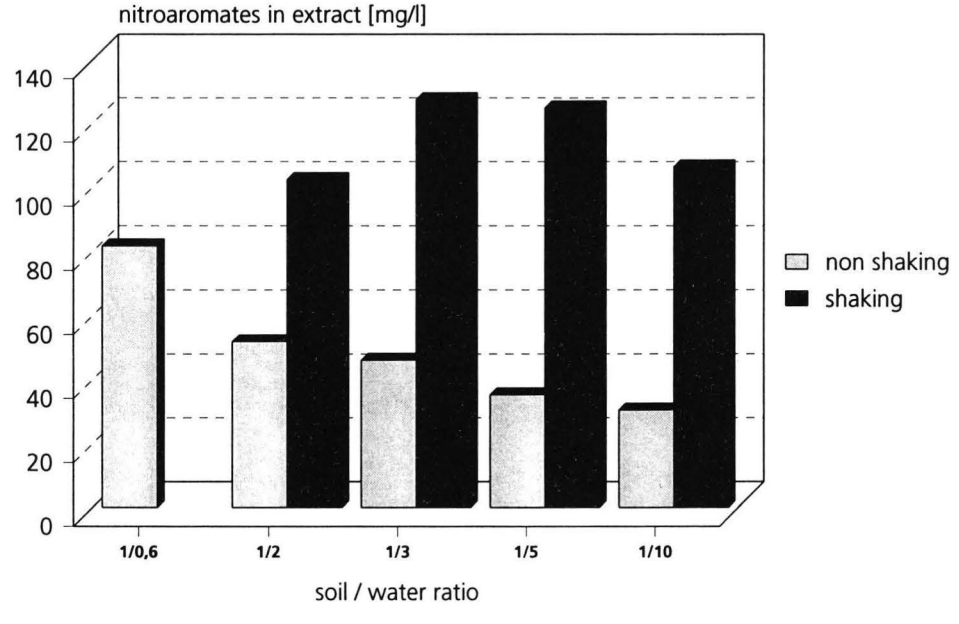

Figure 3.
Variation of soil/water ratio
soil contaminated by nitroaromates

Clean up steps of the soil extracts

Further to the elution method the preparation of the soil extracts is decisive for the subsequent determination of the contaminant concentrations. For heavy metals pressure filtration is usually applied, whereas for organic contaminants this method may result in significantly lower measured concentrations due to sorption to the membranes. Especially for ecotoxicological tests higher amounts of elution solutions are needed depending on the used test organisms. Table 3 presents an overview with respect to the influence of different preparation methods.

Table 3. Influence of different preparation methods on elution yields
(S4-extract; applied amount: 10 mg/kg each)

Preparation	lindane [µg/l]	pyrene [µg/l]	PCP [µg/l]	PCB 52 [µg/l]
settled supernatant after shaking	148	146	236	144
laboratory centrifuge (20 min; 650 g)	59	29	72	9
laboratory centrifuge + glass fibre microfilter 0.7 µm	52	22	70	4
Sorval centrifuge (20 min; 27.800 x g)	43	18	71	5
Sorval centrifuge + glass fibre microfilter + 0.7 µm	43	13	68	2
pressure filtration, membrane filter 1.2 µm	9	11	37	7

The separation of solids by settling leads to a high particle-bound pollutant concentration in the soil extract. These contaminants, however, are not or only partly bioavailable for the test organisms and therefore would result in a theoretical overestimation of the toxicity potential. The particle-bound pollutant portion is significantly reduced by centrifugation and microfiltration. Comparable results are obtained by centrifugation (27.800 x g). Additional microfiltration does not lead to a further improvement of the results. Pressure filtration results in reduced pollutant concentrations due to adsorption to the filter and in the filter cake, respectively. For feasibility reasons either a combination of laboratory centrifuge and glass fibre microfilter (pore size 0.7 µm), and centrifugation in the Sorval centrifuge with at least 20.000 x g is proposed for preparation. According to the specific problem to be solved a combination of two filters can be used. It is essential for the preparation that sorption of the investigated contaminants to the filter materials is tested in each case.

Discussion

The results elucidate that for both - chemical and biological analysis - a soil/water ratio of 1/2 is a quick and easily to standardize method leading to a realistic worst case prediction of a possible groundwater contamination. The predicted concentrations which may leave the characterized soil will be further reduced during their migration through underlaying soil horizons toward groundwater.

For poorly soluble organic soil contaminants like PAHs or long chain hydrocarbons a column method is proposed by a DIN-method (draft). Soil column tests are very time-consuming and difficult to standardize. Moreover, soils with high clay contents have to be mixed with sand to avoid clogging of the columns. First tests on the feasibility and standardadisation of the method in Baden-Württemberg did not yield satisfying results. Therefore, further testing should be done to find out whether the shaking method might be a more time saving and more easily standardizable alternative. In this case the principally higher substance concentration in the soil extract (realistic worst case assessment) can be considered in the results assessment.

Substances posing specific problems in ecotoxicological testing are fairly soluble contaminants, which are solubilized in water only in low concentrations. In soil natural solubilizers are available, as e.g. DOM (humic acids) or biotensides. To increase the solubility of fairly soluble contaminants in some cases detergents are used. These, however, have to be applied to the soil in high concentrations, since a portion of the tenside is sorbed to soil, whereas the concentration of the free portion has to be above the concentration needed for micell formation to increase the solubility of the substances [Pestke et al., 1997]. Also, high portions of sorbed tensides lead to modifications of the soil properties [Wahle and Kördel, 1997]. Therefore, concerning the mobile, bioavailable portion, the environmental relevance of such soil extracts is questionable, and they are primarily suitable to giving a hint on the total toxic potential. Furthermore, humic acid solutions are investigated for the elution of fairly soluble substances [Wahle and Kördel, 1997], which have a considerably higher environmental relevance [Rebhun et al., 1996; Giessel und Kaupenjohann, 1997; Marschner und Bredow, 1997].
A prerequisite for interpretable test results for ecotoxicological tests with soil extracts, however, is that

- the bioavailability of the pollutants in the eluate is not decreased by the solubilizers
- the added components have no ecotoxicological effects
- increased substance concentrations remain in the test solution during the whole test (no sorption to the walls of the test vessels)
- the test medium (e.g. serum proteins in cell cultures) does not decrease the bioavailability of the contaminants.

These criteria have to be considered for the elaboration of a test strategy to yield significant data which are of relevance with respect to a risk assessment of soils and which indicate adverse effects.

Ecotoxicological tests with soil extracts are already widely applied for the assessment of bioavailable contaminants. Previous experiences and approaches to further developments can be summarized as follows:

Suitability
Numerous publications prove that ecotoxicological test procedures yield valuable information completing chemical analyses. For many soils ecotoxicological tests are already applicable on a routine basis. Some specific cases are described in the following paragraphs.
There is agreement that number and selection of the applied test systems depend on the purpose of application. Controls during the course of a remediation measure can be restricted to one sensitive test method. To make more comprehensive statements the application of a test battery is requested. The used test organisms should comprise various trophic levels to ensure that a broad spectrum of pollutants can be detected.

Sensitivity
Test organisms can only indicate bioavailable contaminants in soil extracts if their concentrations are above the no effect concentrations. These concentrations may considerably exceed the chemically-analytically determinable concentrations. The advantage of biological test procedures as compared to chemical, substance specific analyses is their suitability for the unspecific determination of the total of toxic contaminants. To detect also contaminant concentrations lower than no effect concentrations testing with concentrated solutions is performed.

Nutrients in the soil extracts
Soil extracts may contain considerable concentrations of nutrients. Depending on the used test organisms and procedures it may be of importance to consider these additional nutrients. The aspect of nutrient supply is especially important when the original culture medium proposed for the respective test contains significantly lower concentrations of these elements. Nutrient supply also plays a role when populations increase during the test period and are strongly dependent on available nutrient elements (e.g. algae, microorganisms).
Previous investigations indicate that it may not be sufficient to consider only the main nutrients, nitrate and phosphate, by introducing an additional control which contains the same concentrations of these elements as the soil sample. It has been demonstrated that further unknown stimulating substances are present in the soil extracts, which cannot all be detected in routinely performed investigations. As an alternative, complex nutrient solutions could be applied with exceeding concentrations of all nutrient elements. This strategy is being investigated in the scope of a BMBF project "Ecotoxicological Test Batteries" (project sponsored by the German Federal Ministry for Environment, Nature Conservation and Nuclear Safety).

pH values of the soil extracts
The availability/toxicity of contaminants can be influenced by the pH value. Ecotoxicological testing in the scope of chemicals' assessment are therefore conducted at fixed pH values offering optimal conditions for the respective test organism. For eluates of soil samples sometimes pH values are determined which considerably exceed or remain under the optimum value (which is in general pH 7). So far no uniform

approach exists to solve the problem. A feasibile solution could be the performance of parallel tests with such soil extracts considering both, natural and optimal pH values.

Colouring of the eluates
In soils with a high content of humic substances eluates can have a strong brown colour. In such cases it has to be carefully examined whether a detected adverse effect is due to the contaminant or caused by measuring errors resulting from colouring of the soil eluates by eluted humic substances. Colouring can play a role for organisms and test parameters that are influenced by illumination as well as for photometrically determined activities. Possibilities of correcting test results are mainly given with the microtox assay (inhibition of luminescence).

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A RAPID METHOD FOR PREDICTING THE RESIDUAL CONCENTRATION AFTER BIOLOGICAL TREATMENT OF OIL-POLLUTED SOIL

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Key words: characterisation, contaminated soil, mineral oil, biological treatment, bioavailability, biodegradability

SUMMARY

The residual concentration after biological treatment of soil polluted with mineral oil is governed by the biodegradability and the bioavailability of the pollution. Only the fraction of the oil that is both available and degradable can be removed biologically. Based on this concept, a rapid laboratory method to predict the residual concentration is being developed. This method involves two steps. In the first step the amount of bioavailable pollutant is assessed by extraction of the soil with a surfactant solution. Subsequently, in the second step, the biodegradability of the extracted (solubilized) pollutant is determined. To validate the method, the results obtained are compared with those of bench-scale and full-scale biological treatment.

Surfactants were selected based on their aqueous solubility, toxicity, and interference with mineral oil analysis. Preliminary results show a good agreement between the residual mineral oil concentration after surfactant extraction and the residual concentration after bench-scale biological treatment of polluted soil. The method is currently being optimized.

Contaminated Soil '98, Thomas Telford, London, 1998, 251–259

INTRODUCTION

Pollution with mineral oil forms the major part of the soil pollutions that can be cleaned by biological treatment. During a biological treatment, the mineral oil concentration usually shows the following, characteristic pattern: after an initial phase with a high biodegradation rate, the degradation rate drops markedly and eventually, when the biodegradation is almost negligible, an apparent residual concentration is reached.

> The poor predictability of the final residual pollutant concentration is one of the main problems for biological soil remediation.

For enterprises performing biological soil treatment on a regular basis, information on the residual concentration must be available quickly. This excludes the use of conventional methods for assessing bioremediation of polluted soil, which require at least 4 weeks (e.g. Saberiyan et al. 1995, Tabak et al., 1997). In a joint project, MTI Environmental Technology and BSN Soil Remediation are developing a rapid method for predicting the residual mineral oil concentration after (ex-situ) biological remediation of oil-polluted soil.

CONCEPT

For oil-polluted soil, two factors can be identified determining the residual concentration after biological treatment:

1. **Bioavailability.** For biodegradation to occur it is essential that the degrading micro-organisms have access to the pollutant. In soil, hydrophobic organic pollutants such as mineral oil often occur in a physical state in which they are not directly available to the micro-organisms (sorbed, separate phase). In that case the transport of the pollutant to the micro-organism is the factor limiting biodegradation. Since bioavailability is gouverned by physico-chemical processes, it is possible to determine bioavailability with a physico-chemical method (Volkering 1996).

2. **Biodegradability**. Mineral oil is a poorly defined, heterogeneous substance. Although the major part of the oil constituents can easily be degraded by many soil micro-organisms, it is well known that other oil components are persistent to biodegradation (e.g. Riis et al 1997). Common chemical analysis of mineral oil is based on separation by boiling point and provides little information on biodegradability. Norris (1994) advises biodegradability testing prior to each biological treatment of oil-contaminated soil.

In Figure 1 the concept is shown schematically. Fraction I is both biodegradable and bioavailable, and can therefore be removed with biological treatment. The residual concentration will consist of the fractions II, III, and IV.

Accordingly to this concept, the method developed consists of two assays. In the first assay the bioavailable part of the pollutant is extracted with a surfactant-solution; in the second assay the biodegradability of the emulsified pollutant is determined.

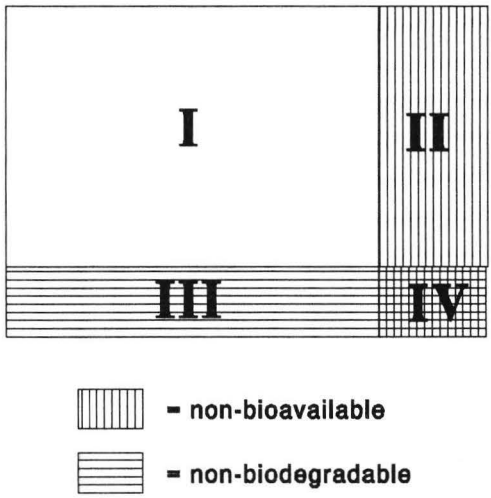

Fig 1: Schematical representation of different fractions of mineral oil pollution in soil

Bioavailability assay

The poorly available part of mineral oil pollutions mostly occurs as a non-aqueous phase liquid (NAPL). The microbial uptake of NAPLs can occur via three mechanisms: (i) uptake of hydrocarbon dissolved in the aqueous phase, (ii) direct uptake of hydrocarbons from the liquid-liquid interface, and (iii) uptake of "pseudosolubilised" hydrocarbons (Hommel 1990). For the last two uptake mechanisms, emulsification of the NAPL is essential. In the direct uptake of NAPLs, the micro-organisms themselves have an emulsifying effect, while pseudosolubilization is caused by the presence of extracellular emulsifying surface-active agents produced by the micro-organisms. It is therefore not surprising that the effect of surface-active agents (surfactants) on the mobilization of organic pollutants is similar to the effect of micro-organisms during biodegradation (Volkering 1996). Therefore, an extraction based on emulsification by a selected surfactant solution is expected to be a suitable assay for assessing the amount of bioavailable pollutant.

Biodegradability assay

When pollutant is present in an emulsified state, transport to the aqueous phase can occur at a high rate. Therefore bioavailability-limitations can be excluded during the biodegradation of emulsified oil in an aqueous system with intensive mixing. Under these conditions, complete degradation of the biodegradable constituents can take place in a short period of time, providing sufficient degrading microorganisms are present.

In the development-phase two different oil-polluted soil samples will be used, the results obtained with these samples will be compared with other laboratory-scale and full-scale treatment. The method will be evaluated by comparing the results of the method with the results of full-scale biological treatment for ten different oil-polluted soil samples.

MATERIALS AND METHODS

Materials. The surfactants tested are listed below; figures in brackets give the hydrophile-lipophile balance (HLB) of the surfactant: Brij 30 (9.7), Brij 35 (16.9), Brij 56 (12.9), 10 Lauryl ether (14.1), Brij 78 (15.3), Sodium dodecyl sulphate or SDS (HLB unknown), Tergitol NP-7 (11.7), Tergitol NP-9 (12.9), Tergitol NP-35 (17.5), Triton X-100 (13.6), Triton X-114 (12.6), Tween 80 (HLB unknown), and a rhamnolipid biosurfactant produced by *Pseudomonas aeruginosa* (HLB unknown). The only soil tested so far is a sandy soil with an organic carbon content of 1% dw. The soil was polluted with 5300 mg/kg dw mineral oil, presumably diesel oil.

Bioavailability assay. The extraction of bioavailable mineral oil was tested by shaking 50 or 100 g of the oil-polluted soil with 500 ml of a solution containing 0.5-4.0% (w/v) of different surfactants. After a shaking time of 0.5-24h at 25°C the extraction was stopped by centrifuging the slurry at 5.000 g for 60 min. The liquid phase was removed by decanting and the mineral oil concentration of the liquid and/or solid phase was determined. In some experiments the extraction was repeated.

Biodegradability assay. Biodegradation of 0.05, 0.1 or 0.2 % w/v diesel oil in mineral medium or emulsified in 0.1 or 1.0 % w/v surfactant-solutions (Brij 35 and Triton X-100 only) was tested by incubating 100 ml of the fluid in 500 ml serum flasks. After inoculation with 10 ml of an active oil-degrading continuous culture, the flasks were incubated on a rotary shaker (125 rpm) at 25°C for a period of two weeks. The course of the biodegradation process was followed by measurement of the optical density at 660 nm. The toxicity of the surfactants was tested by following bacterial growth on acetate in the same setup as described above for diesel oil.

Bioremediation. Bench-scale bioremediation was performed at small scale and at medium scale. Small-scale experiments were done at 25°C with 50 gr of nutrient-amended soil, incubated in air-tight 500-ml serum flasks. Degradation was followed by O_2 consumption and CO_2 production. For the medium-scale experiments, 5.5 kg of nutrient-amended soil was incubated at 25°C in a column (H/D = 6) flushed with air (400 ml/min). The concentrations of CO_2 and O_2 in the off-gas were followed. Every two weeks a sample of the soil was taken for analysis of the mineral oil content.

Full-scale landfarming was performed with 50 tons of the oil-polluted sandy soil. Nutrients (ammonium, phosphate) were added and the soil was piled to an average height of 1.2 m. The soil was tilled every two weeks; the temperature was not controlled.

Analysis. Mineral oil was analyzed by standard GC-FID measurement after an adapted extraction procedure developed for extraction of mineral oil from surfactant-solutions. Concentrations of CO_2 and O_2 in the gas-phase were analyzed using a Geotechnical Instruments Anagas CD 95 gas analyzer.

RESULTS AND DISCUSSION

Having been started recently, the project is still in the developing phase. The results published here represent preliminary data of the laboratory experiments.

Surfactant selection

As yet a total of 7 different surfactants has been tested, having a hydrophile-lipophile balance in the range from 9 to 18. SDS and the rhamnolipid biosurfactant were the only ionic surfactants, the other surfactants were all of the nonionic type. The surfactants were tested on (i) water solubility, (ii) toxicity and (iii) interference with the hexane extraction for mineral oil analysis. All of the surfactants tested were soluble in water. Toxicity testing showed Brij 35 and Triton X-100 not to inhibit growth on acetate and diesel oil. The results of the toxicity tests with the other surfactants are not yet available at present. For the nonionic surfactants interference with the hexane extraction could be prevented by addition of ethanol during the extraction procedure; the interference caused by the anionic SDS and the rhamnolipid biosurfactant could be prevented by acidification of the aqueous phase.

Bioavailability assay

Of the factors affecting the extraction of the available mineral oil, the following have been investigated: type and concentration of the surfactant, extraction time, liquid/solid ratio, and the amount of extraction steps. At the moment of writing, the bioavailability assay is still being optimized. Initial extraction experiments with different surfactants at concentrations of 0.5-2.0% w/v resulted in low amounts of extractable oil and a poor recovery ($\pm$ 60%). This could not be improved significantly by altering the extraction time, changing the liquid/soil ratio, or performing a double extraction. Additional experiments (performed with Triton X-100 only) demonstrated the poor recovery to be caused by the presence of fine particles in the liquid phase after centrifuging. The residual oil concentration after improved extraction with 1% w/w Triton X-100 solution was 500 mg/kg dw; the mineral oil recovery was 102%.

The amount of oil extracted in initial experiments tended to increase with increasing surfactant HLB, as shown in Figure 2 on the next page. Surfactants with a higher hydrophile-lipophile balance are more hydrophile, which may cause an improved contact with the soil and penetration of small pores compared to more hydrophobic surfactants. It should be noticed that Figure 2 presents only the data obtained with the nonionic alcohol ethoxylate or alkylphenol ethoxylate surfactants. The extraction results obtained with the other surfactants were in the same range, but could not be related to the HLB number.

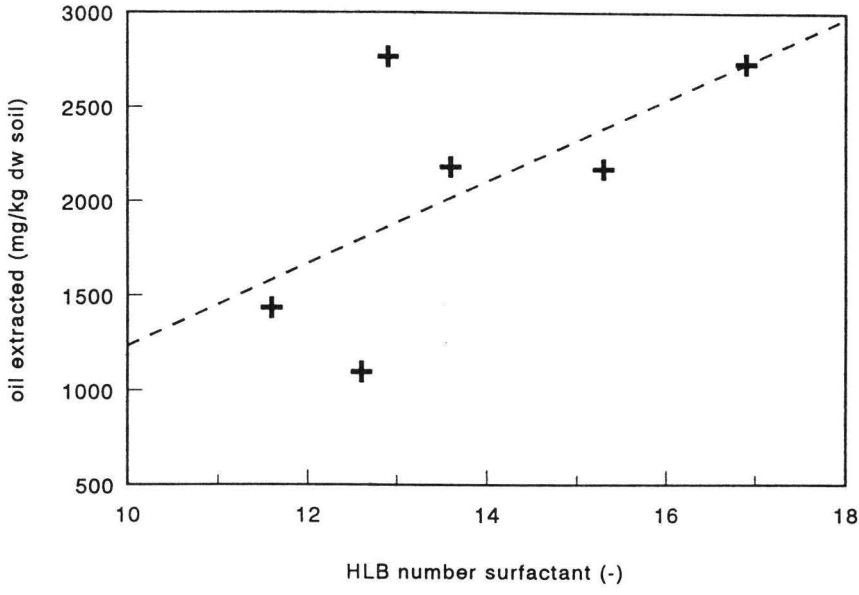

Fig 2: Mineral oil extracted with 1% w/v solution of different surfactants as a function of surfactant HLB.

Biodegradability assay

The first tests for the assay to determine the biodegradability of the bioavailable part of the mineral oil were performed with diesel oil in mineral medium or emulsified in solutions containing the different surfactants. In all cases the biomass production was considerable. A slightly shorter lag-phase was observed in the experiments with surfactants than in those without surfactants. In the experiments with Triton X-100 the biomass production showed a dual-phase behaviour typical for diauxic growth. It was concluded that after the mineral oil was degraded, the microorganisms started degrading the surfactant. In the experiments with Brij 35 the biomass production rate was higher than in the absence of the surfactant during the entire growth phase, indicating that the diesel oil and the surfactant were degraded simultaneously. Figure 3 gives an example of some typical growth curves.

From the course of the growth curves, biodegradation of the mineral oil was concluded to be completed within one week, even in the absence of surfactants. In future experiments, this assumption will be checked by determination of residual mineral oil concentations. The assumed rapid biodegradation allows the execution of the total method to be completed within one week.

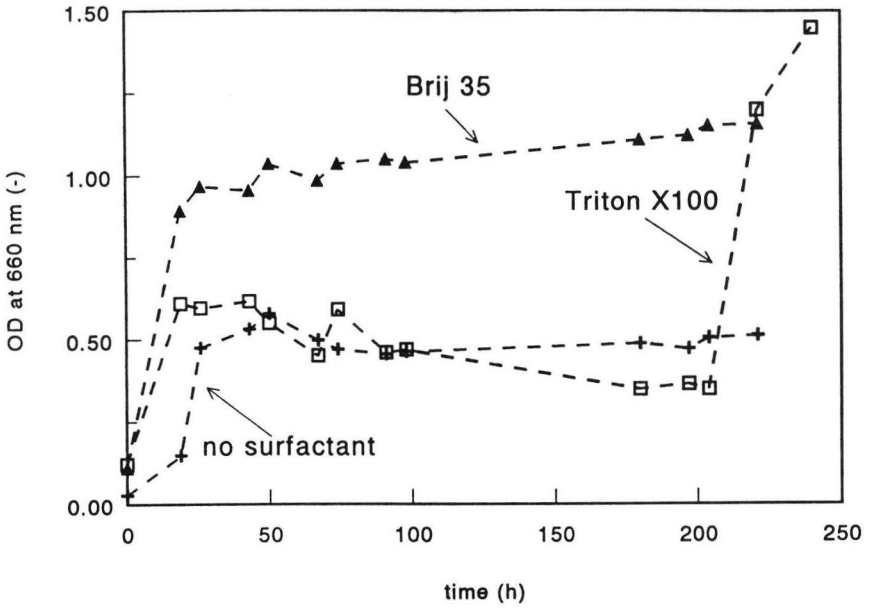

Fig 3: Biomass production during biodegradation of diesel oil in mineral medium and of diesel oil solubilised in 1% w/v solutions of Triton X-100 and Brij 35

Comparison with bench-scale and full-scale bioremediation

Both full-scale and bench-scale bioremediation showed the oil pollution to be readily biodegradable. The full-scale treatment is still being continued at present. The mineral oil concentration after four weeks of small-scale treatment was 1100 mg/kg dw, the residual concentration after 10 weeks was found to be 450 mg/kg dw. The medium-scale treatment is also still being continued; the mineral oil content after two weeks was 1300 mg/kg dw. Initial degradation rates in both the small-scale and medium-scale experiments were high (160, respectively 265 mg/kg dw.day). The residual concentration after extraction with 1.0% Triton X-100 solution is 500 mg/kg dw. In Figure 4 the GC-chromatogram of the initial oil pollution (A) is compared with the residual oil pollution after 10 weeks of small-scale treatment (B), and the residual oil concentration after surfactant extraction (C). It can be seen that the residual concentration after surfactant extraction is in the same range as the one after bench-scale treatment. Compared to the chromatogram after biodegradation (B), the chromatogram after surfactant extraction (C) shows slightly higher concentrations of mineral oil components with a retention time of 400-800 s (equivalent with linear alkanes C12-C18). This difference will be investigated in future surfactant extraction experiments.

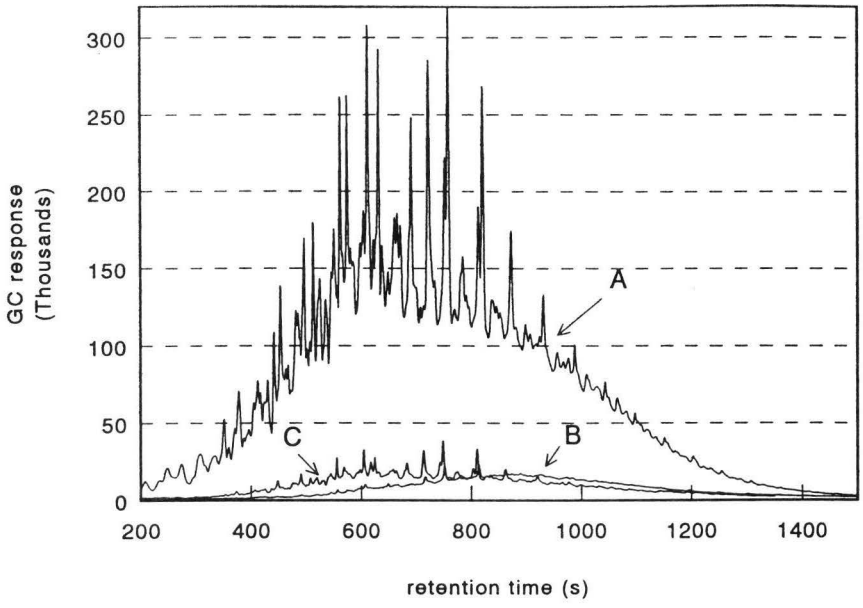

Fig 4: GC chromatorgam of mineral oil in polluted soil (A), in soil after biological treament (B), and in soil after surfactant extraction (C).

CONCLUSIONS

Although the rapid method for determining the residual concentration after biological soil remediation is still in the developing phase, the results obtained so far are promising. The interference of surfactants with the hexane extraction for mineral oil analysis can be prevented for both nonionic and anionic surfactants. The surfactants tested did not cause inhibition of bacterial growth on acetate and diesel oil. Extraction experiments with surfactants demonstrated the residual oil concentration to be in the same range as the concentration after bench-scale treatment. More importantly, similar GC-chromatography patterns were found. Biodegradation of oil emulsified in surfactant solutions was completed within one week, enabling the method to be as rapid as required.

ACKNOWLEDGEMENTS

This project was partly funded by NOVEM, the Dutch research programme for energy and environment. Rhamnolipid biosurfactant was kindly supplied by drs W.H. Noordman of the Biochemical Department, University of Groningen. M.A.H Smits is thanked for technical assistance.

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Methods for Chemical Analysis of Contaminated Soil Samples - Tests of their Reproducibility Between Nordic Laboratories

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ABSTRACT

In an effort to develop common analytical methods for contaminated soil samples the Environmental Authorities of the Nordic countries have together with Nordtest published the report *Nordic Guidelines for Chemical Analysis of Contaminated Soil Samples*. The aim of these guidelines has been to describe analytical methods which could be accepted in all the Nordic countries and in that way contribute to reduce the variation in the analytical results between laboratories. The methods covered reflect the environmental concerns and priorities in the Nordic countries for the time being, i.e. Heavy Metals, Chlorophenols, Creosote, Volatile Organic Compounds, PCB, THC and PAH.

The repeatability and reproducibility of the Guideline methods were determined in a Nordic inter-laboratory test in 1996, and the results showed some variations. The analytical methods and the results from the inter-laboratory tests are given for Heavy Metals, Chlorophenols, Creosote, Volatile Organic Compounds and PCB.

INTRODUCTION

Extensive work has been and is being done to identify and cleanup landfills and hazardous "waste" contaminated sites, the so called "past sins", in the Nordic countries. When facing the large costs for cleaning up contaminated sites, it is necessary for the chemical analysis that provide the foundations for cleanup efforts to be comparable, reproducible and reliable.

Sample treatment and preparation, along with chemical analysis are often performed differently at different laboratories and may provide different results, despite the fact that some of these laboratories are accredited. It was therefore a priority to develop complete guidelines that could contribute to make the results comparable and reproducible even when the analyses are performed in different laboratories in the Nordic countries. This is especially important when the effects of remedial action need to be verified.

An environmental survey of a site will be done in order to obtain information about the kind, extent and distribution of contaminants, and if needed, to select the most appropriate cleanup

Contaminated Soil '98, Thomas Telford, London, 1998, 261–278

methods. Guidelines for *soil investigations* have already been developed in Denmark, Finland, Norway and Sweden (Assmuth et. al, 1992; Norwegian Pollution Control Authority, 1997; Swedish Environmental Protection Agency, 1995). These guidelines give appropriate methods for sampling and are meant to be used for planning, executing and reporting these types of environmental surveys.

Samples from such survey's (soil, ground water, leachate, air, etc.) are sent to an analytical laboratory for chemical analyses in order to ascertain the composition of the polluting contaminants. The results from the analyses will in turn be used when deciding upon further action. For example, if high concentrations of environmentally hazardous compounds are found, costly cleanup efforts may be initiated, while any further activity can be halted and the site declared acceptable if low concentrations are found. Errors in the results from such analysis can have environmental and economic consequences.

Advanced chemical analyses are complicated to perform and can be fraught with error. These errors can be minimised, however, with adequate routines. Another uncertainty factor which can be eliminated, is the use of different methods or conditions for the same analysis at different laboratories. However, the laboratories should still have the opportunity to use their own or alternative methods, but this should preferably be validated and compared with the proposed method in the Guideline, to give an estimate of the performance.

The Nordic Guidelines (Karstensen, 1997) describes methods for Heavy Metals, Chlorophenols, Creosote, Volatile Organic Compounds, PCB, THC and PAH, and covers also Quality Assurance, Sampling Strategy and Validation. The analytical methods is first of all based on the already existing national or international standards, i.e. ISO/TC 190 and various CEN standards, and/or on common practise.

The repeatability and reproducibility of the proposed methods in this Guideline were determined in a Nordic inter-laboratory test according to ISO 5725-2.

ANALYTICAL METHODS

The following paragraphs give a brief description of the analytical methods for the determination of Heavy Metals, Chlorophenols, Creosote, Volatile Organic Compounds and PCB.

Heavy metals: As, Cd, Cr, Cu, Hg, Ni, Pb and Zn

The method for determination of heavy metals is a partial digestion method using air dried (24 hours) and sieved (< 2 mm) samples. Approximately 1 g of the dried sub sample is introduced into a 100 ml digestion bottle, made of uncoloured Pyrex glass with polypropylene screw caps or suitable closures. Bottles and closures should be able to resist a temperature of 120°C and a pressure of 200 kPa. 20 ml of 7 M nitric acid (HNO_3) is added and the mixture is heated in an autoclave at 120°C (200 kPa) for 30 minutes. The solution is cooled, filtered and transferred to a 100 ml flask, diluted with distilled or deionized water. The solution should be transferred to a plastic bottle prior to instrumental analysis. Blank solutions is prepared in the same way. Alternatively, samples could be digested in polytetrafluoroethylene (PTFE) bombs, heated in a microwave oven. The laboratory is free to choose the instrumental methods for determination of the analytes.

Chlorophenols
Field moist soil samples are extracted with acidic acetone:hexane (1:1) by sonication for 6x2 min during an hour. The clear part of the mixture shall further be extracted two times with NaOH and acidified by HCl. The extract shall then be extracted twice with hexane, and the hexane phase further extracted two times with K_2CO_3. The chlorophenols in the alkaline extract shall then be acetylated by acetic anhydride, after which the acetylated chlorophenols are extracted with hexane. The extract shall be dried using Na_2SO_4. Chlorophenols in the hexane phase are determined by gas chromatography using a dual column system and electron capture detection. The calibration is based on peak height and on the response of an internal standard, 2,4,6-tribromophenol.

Creosote
Soil samples are extracted with acetone including internal standard by rotation for one hour. The supernatant is removed after centrifugation. This procedure is repeated once and the organic phases are combined and evaporated to 2-4 ml with nitrogen. An equal volume of water is added and the extract is extracted twice with 5 ml of n-hexane. The hexane phases are combined and evaporated to a volume of about 1-2 ml. The target compounds are determined by GC-FID.

The target compounds in the analyses of creosote in soil are the following:

PAH:	naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, biphenyl, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene and benzo(a)pyrene.
Phenols:	o-cresol and p-cresol.
O-heterocyclics:	dibenzofuran.
N-heterocyclics:	carbazole.
S-heterocyclics:	dibenzothiophene

Volatile organic compounds - VOC
The Guideline describes two methods, with no preference to one or the other. Method 1 is based on solvent extraction. Internal standards and the extraction solvent (pentane) are introduced through the vial septum. The solvent/soil mixture is shaken manually until a slurry is obtained, then treated for a minimum of 5 minutes in an ultrasonic bath, and extracted for at least 45 minutes on a mechanical shaker. The pentane extract is isolated after addition of pH 2 water, and after drying with sodium sulphate, analysed with gas chromatography/mass spectrometry (GC/MS).

Method 2 is performed according to the EPA method 8260 "Gas Chromatography/Mass Spectrometry for Volatile Organics" (EPA, 1986), which includes a Purge & Trap extraction of the VOC from the soil. Internal standards are introduced through the vial septum. An aliquot of the methanol extract is diluted with water containing internal standards and analysed. The dilution factor depends on the expected VOC levels. With VOC levels in the

1-10 mg/kg range a 1:10 dilution may be appropriate. At higher concentrations a 1:100 dilution factor may be used. The water/methanol phase is analysed by purge-and-trap as if the original sample was water. The VOC content is determined by GC/MS.

PCB

Dry samples are moistened with water. Prior to extraction recovery standards (PCBs 53, 112, 198; 100-1000 ng depending on level of contamination) are added and the samples shaken gently to mix. Acetone (3-5 ml/g) is added, the samples are sonicated for 5 min and then shaken vigorously for 1 hr. After repeating the extraction with acetone:hexane (1:3) (3-5 ml/g) the organic phases are washed with 50 ml of 0.2M NaCl/0.1M H_3PO_4. After separation the water phase is washed twice with 10 ml hexan:diethylether (9:1) and the organic phases are combined and evaporated almost to dryness at 60°C in a waterbath. The samples are cleaned with H_2SO_4 (conc.) and/or with TBA to remove sulphur and/or the samples are fractionated by silica gel.

The individual PCB congeners are analysed by GC-ECD or GC-MSD with 60m capillary columns of two polarities. GC-conditions should be optimised in respective laboratories but could for example be: injector 270°, ECD 290°, MSD interface 290°; oven 85° for 2 min, 30°/min to 210°, hold 28 min, 2°/min to 250°, 7°/min to 280° (DB1701) or 310° (DB5), hold as necessary to elute PCB 209. A long isothermal period early in the temperature program is necessary to separate components like PCB 28 and PCB 31.

Prior to injection, the sample is dissolved in isooctane containing the injection standard (for example tetrachloronaphtalene). The calibration is based on peak height of individual PCBs/peak height of the injection standard. Detection limits will vary with amount and type of contamination. It should be close to 10 µg/kg for each congener but needs to be determined on a case to case basis.

INTER-LABORATORY TESTS

All laboratories in the Nordic countries which analyse heavy metals and organic pollutants in contaminated soil, were invited to take part in the inter-laboratory test. The invitation was sent out to more than 90 laboratories.

The inter-laboratory test was arranged as a test of repeatability and reproducibility of a standard measurement method. The statistical treatment was performed according to the international standard ISO 5725-2, First edition 1994-12-15: "Accuracy (trueness and precision) of measurement methods and results, Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method" (ISO, 1994).

A balanced uniform level experiment was performed. The aim was to test one or two different levels of contamination in soil and one test solution, each with three replicates. Each group of replicate measurements (n=3) belonging to one level should be carried out under repeatability conditions, i.e. within a short interval of time and by the same operator. The statistical program involved the testing of the within-laboratory standard variances by Cohran`s test and the testing of the variation of means by Grubb`s test after which statistical outliers were excluded for the final calculation of the repeatability and reproducibility of the method. Some datasets contained some extreme values which could be due to the use of

incorrect units, dilution errors and lack of analytical performance. These extreme values were rejected from the dataset before calculation.

Symbols and abbreviation used in the following tables:

Level j	sample types (described for each parameter)
N	number of laboratories participating (or replicates)
pj	number of laboratories used for calculation
mj	mean value (for solid samples mg/kg, for solutions mg/l)
S_r	standard deviation within laboratory (the repeatability)
S_R	standard deviation for the reproducibility
CV_r	the variation coefficient within laboratory (in %)
CV_R	total variation coefficient reproducibility (in %)
Ref. value	reference value, for certified reference materials or solutions

Heavy metals

Two real soil samples (samples A and B), one certified reference soil sample (sample C: CRM 021-100) and one standard solution (sample D) were tested (Rustad, 1997).

The real soil samples were sandy soil obtained from sites of polluted soil in Norway. The two real soil samples were air-dried at room temperature. Coarse material (e.g. stones) was removed manually, after which the material was sieved through a 2 mm sieve, followed by sieving through a 500 µm sieve. The real soil samples were mixed for several days using a tumbler. The homogeneity was checked by randomly taking 8 subsamples prepared as wax pellets and subsequent determination of Cr, Fe, Ni, Cu, Zn and Pb with x-ray fluorescensspectrometry. This homogeneity test revealed that the spread among the test samples for most of the measured elements was less than 5%.

The reference material (C) was used as received, without any further homogenisation. The dry matter content was 98.8%, 98.8% and 99.7% for samples A, B and C, respectively. The organic matter content (determined as loss of ignition; 2h ignition at 550°C) was 5.9%, 7% and 2% for samples A, B and C, respectively.

The soil samples were polluted with an unknown level of the heavy metals. The standard solution (D) containing As, Cd, Cr, Cu, Hg, Ni, Pb and Zn was prepared in water using 1000 ppm certified solutions of the individual elements and diluting the mixture to a final volume of 2.5l and adjusting the matrix to 5% HNO_3.

Each laboratory received 25g of sample A and B, 8g of sample C and 100ml of sample D. The soil samples were sent out in small plastic bags, tightly closed, and the test solution in a screw-capped plastic bottle. The samples were sent out on May 2, 1996, and the last date of accepted results was June 30.

The samples were also analysed by the producers laboratory according to the Guideline method. The relative standard deviation within the laboratory (the coefficient of variation, CV_r) varied between 2% and 10% for soil A and B and between 7% and 22% for soil C (Table 1). The larger spread in sample C is due to some inhomogenity in the sample itself, as was clearly revealed by analysing two different boxes of the reference material.

Table 1 Repeatability results of heavy metals within the producers lab.

Element	Level j	N	m_j	S_{rj}	CV_r	Ref. value
As	A	10	7.3	0.61	8.3	
	B	10	200	12.3	6.2	
	C	10	39.4	3.1	7.9	24.8
Cd	A	6	2.45	0.13	5.5	
	B	6	2.07	0.18	8.9	
	C	11	1.26	0.10	7.8	1.20
Cr	A	11	29.4	0.83	2.8	
	B	11	37.6	0.71	1.9	
	C	10	10.6	2.4	22.6	10.70
Cu	A	10	136	11.8	8.7	
	B	11	533	22	4.2	
	C	10	4797	596	12.4	4792.4
Hg	A	6	0.36	0.06	16.3	
	B	6	0.49	0.07	13.6	
	C	6	4.5	0.5	11.1	4.7
Ni	A	11	30.3	1.0	3.3	
	B	11	45.7	1.5	3.3	
	C	11	12.7	1.7	13.3	12.6
Pb	A	10	167	10.7	6.4	
	B	11	575	62	10.8	
	C	11	238882	19854	8.3	114742.4*
Zn	A	11	881	42.8	4	
	B	11	1565	62	10.8	
	C	10	583	64	11.1	546.4

* (indicated value)

Thirty-eight laboratories from Denmark (13), Finland (11), Island (2), Norway (7) and Sweden (5) took part in the inter-laboratory test for heavy metals. Two of the laboratories participated only with their own method and five laboratories performed their own method in addition to the Guideline method. The majority of the participants submitted full datasets with the exception of As and Hg where relatively fewer data were submitted. The results of this test are summarised in Table 2.

The overall performance on the test solution was good with a total coefficient of variation CV_R between 3.73% for Cu to 13.9% for Hg. The laboratories seem to have larger difficulties analysing As and Hg than the other elements. 90 % of the laboratories were able to analyse the test solution within 25% of the assigned values for Cd, Cr, Cu, Ni, Pb and Zn and around 80% of the laboratories were able to analyse the test solution for the same elements within 10% of the assigned values. For As and Hg respectively 85% and 80% of the laboratories were able to analyse within 25% and 55% and 40% within 10% of the assigned values.

For the soil samples the coefficient of variation CV_R varied between 6% to 26% for soil A and B, and between 6% to 40% for soil C. Around 85% of the laboratories were able to analyse the soil samples within 25% of the assigned values for all the elements except As and Hg. Around 65% of the laboratories were able to analyse As and Hg within 25% of assigned values. The exception was the level of high content of As in soil B, which was analysed satisfactory by 85 % of the participants.

Table 2 Inter-laboratory test results for heavy metals

Element	Level j	N	pj	mj	S_{rj}	CV_r	S_{Rj}	CV_R	Ref.val.
As	A	29	24	7.2	0.43	5.9	2.2	30.1	
	B	29	26	198	14.5	7.3	32	16.1	
	C	28	21	34.6	2.4	7.1	9.9	28.6	24.8
	Solution	29	21	0.249	0.01	4.4	0.02	9.1	0.25
Cd	A	36	33	2.3	0.16	7.0	0.48	20.7	
	B	36	29	2.0	0.15	7.5	0.45	22.7	
	C	36	30	1.5	0.11	7.6	0.21	14.5	1.20
	Solution	37	27	0.29	0.005	1.8	0.023	7.9	0.30
Cr	A	36	34	29.4	1.7	5.9	5.1	17.3	
	B	36	31	36.5	1.1	2.9	6.0	16.6	
	C	35	30	10.0	0.6	6.3	2.5	24.8	10.70
	Solution	37	28	1.76	0.03	1.6	0.12	6.8	1.75
Cu	A	35	32	130	8.6	6.6	14.0	10.8	
	B	35	30	524	23.0	4.4	43.0	8.2	
	C	33	25	4461	294	6.6	556	12.5	4792.4
	Solution	36	23	2.5	0.02	0.77	0.09	3.7	2.50
Hg	A	28	25	0.30	0.017	5.5	0.07	23.6	
	B	28	25	0.46	0.03	7.0	0.11	24.1	
	C	28	19	3.7	0.18	5.0	1.5	40.9	4.7
	Solution	23	15	0.095	0.005	5.1	0.013	13.9	0.100
Ni	A	36	34	30.1	1.2	4.0	3.3	10.8	
	B	36	32	46.0	1.3	2.8	5.3	11.6	
	C	36	29	12.3	1.1	9.2	1.9	15.4	12.6
	Solution	38	27	2.03	0.02	1.0	0.13	6.3	2.00
Pb	A	36	30	170	16.8	9.9	28.4	16.7	
	B	36	30	585	33.9	5.8	58.5	10.0	
	C	36	29	248889	11910	4.8	15845	6.4	114742*
	Solution	37	27	4.13	0.08	1.9	0.26	6.3	4.30
Zn	A	36	34	885	23.9	2.7	51.3	5.8	
	B	36	32	1555	52	3.3	105	6.8	
	C	36	25	562	57.9	10.3	66.3	11.8	546.4
	Solution	38	28	14.6	0.13	0.09	0.63	4.3	15.00

* indicated value

Soil C gave a higher coefficient of variation CV_R than soil A and B. This reflect a larger degree of inhomogenity of the soil sample C itself. The number of outliers were between 1 and 6, indicating systematic errors in some laboratories. Poor performance on the standard solutions was often reflected in the results for the soil samples.

Five laboratories tested their own method in addition to the Guideline method and two laboratories tested their own method only. Three laboratories digested the sample in aqua regia, two used a mixture of HNO_3/H_2O_2, one used 10% HNO_3, and one used a 5g sample in concentrated HNO_3. Some of these laboratories reported results "out of range". In general, however, no significant differences were found between the Nordtest method and the own methods.

Chlorophenols

Three real soil samples (samples A, B and C) and one standard solution (sample D) was used in the inter-laboratory test (Kalevi, 1997). The real soil samples were obtained from a sawmill

site. They were sieved through an 8 mm sieve. The dry matter content was 80.0%, 78.9% and 75.6% for samples A, B and C, respectively. The organic matter content was 5.3%, 5.6% and 9.3% for samples A, B and C, respectively. Sample A was of the same batch as sample B, but it was spiked with 2 mg/kg of 2,4,6 trichlorophenol (TCP), 2 mg/kg of 2,3,4,6-tetrachlorophenol (TeCP), and 5 mg/kg of pentachlorophenol (PCP). The soil samples had a natural content of more than 16 different chlorophenol congeners. The samples were homogenised in a tray and then subsampled into glass jars. Sample D was prepared in water from stock solutions of 16 different chlorophenol congeners. The homogeneity of the samples was tested and the coefficient of variation varied between 1.3% and 21.6% (Table 3).

Table 3. Homogeneity of samples used in the inter-laboratory test (n=5-10)

Sample	246-TCP		2346-TeCP		PCP	
	mj	CV_r	mj	CV_r	mj	CV_r
A	0.19	8.2	1.95	9.6	4.9	12.2
B	0.08	18.3	2.8	21.6	1.4	15.8
C	0.74	2.3	208	10.3	1500	6.7
Solution	47.8	4.1	47.6	1.3	171	5.0

Table 4. Inter-laboratory test results for chlorophenols.

Compound	Level j	N	pj	mj	S_{rl}	CV_r	S_{Rl}	CV_R	Ref.value
2,4,6-TCP	A	18	16	0.253	0.027	10.6	0.081	31.8	
	B	17	15	0.083	0.014	17.0	0.034	40.8	
	C	16	13	1.98	0.244	12.4	1.40	71.1	
	Solution	17	14	53.4	2.80	5.24	9.26	17.3	60
2,3,4,6-TeCP	A	19	17	2.33	0.266	11.4	1.11	47.9	
	B	19	16	2.22	0.271	12.2	1.06	47.6	
	C	19	17	193	38.4	19.9	110	56.9	
	Solution	16	13	52.8	2.32	4.4	18.0	34.1	60
PCP	A	20	19	5.85	0.548	9.4	2.34	40.0	
	B	20	17	1.36	0.212	15.5	0.443	32.4	
	C	18	15	1418	183	12.9	646	45.6	
	Solution	17	14	158	12.7	8.1	51.9	32.9	200

Twenty laboratories from Denmark (4), Finland (10), Norway (1) and Sweden (5) participated in the inter-laboratory test. Several laboratories reported results for up to 16 different chlorophenol congeners, but the majority reported results only for 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol and pentachlorophenol. The number of data only allows statistical handling of the data for these three compounds. The results are given in Table 4.

Creosote

Three samples were sent to the participants (Nylund, 1996). One creosote contaminated soil and two extracts in n-hexane from the soil. The soil was collected in Sweden at an old impregnation site. It was dried in a fume hood and then sieved through a 2mm sieve. The dry weight was 99.7%. Before sending the soil sample to the participants it was tested for homogeneity. The standard deviation of the determination of the target compounds in 15 subsamples was between 4.5% and 10.8%. The two soil extracts were spiked with compounds which originally were present at low concentrations in the soil. The variation for the solutions was between 1.1% and 6.0%. The concentrations of the target compounds were between n.d. to 51 mg/kg.

Twelve laboratories reported results, Denmark (4), Finland (2), Norway (1) and Sweden (5). Five laboratories participated with their own methods. One laboratory used its own method only. The results are summarised in Table 5. The results clearly show that the subsampling and/or extraction step is critical, the soil sample (sample A) showing a variation that is approximately a factor of two larger than that of the solutions. The highest variation was seen for the compounds present at the lowest concentrations. The within laboratory variation was quite acceptable, although there is room for improvement especially for the soil sample.

The between laboratory variation was quite large, probably due to a number of reasons. For instance, the 60% variation for naphthalene in the soil sample is likely explained by evaporative losses being controlled to a varying degree among the laboratories. In addition, the high variation for benzo(e)pyrene in sample B and C may be explained by differing chromatographic performance, since imperfections in the chromatographic systems primarily are reflected in high variations for the higher molecular species (and those present at low concentrations). Another plausible reason for high between laboratory variations is the fact that the laboratories used their own calibration solutions.

A comparison between the Guideline method and the laboratories own methods, showed that the results were quite similar, with a tendency for the recommended method to give somewhat higher yields (at the order of 10%) for the lower molecular weight compounds, which also were present in higher concentrations. It should be taken into account, however, that the statistical basis for this statement is rather weak.

Table 5. The interlaboratory test results for creosote

Compound	Level j	N	p_j^{-1}	mj	S_r	CV_r	S_R	CV_R
o-cresol	Soil A	8	1	0.33	0.086	26.4		
	Extract C	8	8	7.8	0.34	4.3	2.2	27.5
p-cresol	Soil A	8	1	0.49	0.14	28.5		
	Extract C	8	8	7.4	0.46	6.2	1.6	21.5
naphthalene	Soil A	11	6	0.16	0.034	21.1	0.099	60.7
	Extract B	12	11	12	0.70	5.8	2.9	24.1
	Extract C	12	7	0.35	0.011	3.2	0.096	27.2
2-methyl-	Soil A	11	5	0.062	0.008	13.4	0.022	36.2
naphthalene	Extract B	11	7	13	0.19	1.5	1.1	8.6
	Extract C	11	5	0.25	0.010	3.9	0.072	28.2
1-methyl-	Soil A	10	5	0.097	0.007	7.6	0.021	21.6
naphthalene	Extract B	10	8	21	0.32	1.5	4.1	19.8
	Extract C	10	5	0.23	0.011	4.8	0.062	27.2
biphenyl	Soil A	9	5	0.17	0.007	4.0	0.043	25.3
	Extract B	10	7	0.49	0.027	5.5	0.12	25.6
	Extract C	10	6	0.41	0.016	4.0	0.11	27.6
acenaphthene	Soil A	11	11	2.5	0.18	7.4	0.54	22.0
	Extract B	12	12	6.2	0.49	8.0	1.0	16.7
	Extract C	12	9	5.5	0.13	2.3	1.0	18.7
dibenzofuran	Soil A	9	9	2.6	0.20	7.7	0.47	18.3
	Extract B	10	9	6.5	0.59	9.1	1.1	16.6
	Extract C	10	6	6.2	0.16	2.6	0.42	6.8
fluorene	Soil A	11	11	6.1	0.46	7.5	1.8	29.2
	Extract B	12	9	14	0.19	1.4	2.1	15.3
	Extract C	12	11	13	0.60	4.5	2.6	19.8
dibenzo-	Soil A	9	9	2.1	0.20	9.4	0.42	19.6
thiophene	Extract B	9	8	4.5	0.18	4.1	0.99	22.2
	Extract C	9	9	4.6	0.18	3.9	1.3	28.0
phenanthrene	Soil A	11	11	25	1.4	5.4	6.8	26.6
	Extract B	12	10	51	1.5	2.8	8.9	17.3
	Extract C	12	12	49	1.9	3.8	9.1	18.6
anthracene	Soil A	11	9	4.9	0.65	13.3	1.6	33.5
	Extract B	12	11	17	0.69	4.1	3.1	17.9
	Extract C	12	12	16	0.72	4.6	2.7	16.9
carbazole	Soil A	9	9	1.1	0.14	12.9	0.28	25.6
	Extract B	10	10	3.5	0.41	11.4	1.0	28.9
	Extract C	10	9	3.6	0.16	4.5	0.74	20.4
fluoranthene	Soil A	11	11	16	0.83	5.3	4.5	28.5
	Extract B	12	12	31	1.6	5.2	7.9	25.6
	Extract C	12	11	26	0.84	3.2	2.9	11.4
pyrene	Soil A	11	11	9.5	0.71	7.5	2.4	25.4
	Extract B	12	12	19	0.97	5.2	4.6	24.9
	Extract C	12	12	17	0.63	3.7	3.4	20.0
benz(a)-	Soil A	11	11	2.4	0.16	6.6	0.59	25.0
anthracene	Extract B	12	12	4.9	0.43	8.7	1.3	26.4
	Extract C	12	11	4.6	0.15	3.2	0.66	14.5
chrysene	Soil A	11	11	2.2	0.13	5.9	0.46	20.9
	Extract B	12	12	4.8	0.35	7.3	1.2	24.0
	Extract C	12	12	4.4	0.20	4.4	0.74	16.9
benzo(b)-	Soil A	7	7	0.82	0.077	9.4	0.37	45.1
fluoranthene	Extract B	8	8	13	1.2	9.5	3.3	26.3

	Extract C	8	7	1.7	0.081	4.7	0.68	40.0
Compound	Level j	N	pj^1	mj	S_r	CV_r	S_R	CV_R
benzo(k)-	Soil A	6	6	0.74	0.079	10.8	0.22	30.5
fluoranthene	Extract B	7	7	8.9	0.60	6.8	2.3	26.2
	Extract C	7	7	1.4	0.074	5.3	0.65	47.3
benzo(b+k)-	Soil A	10	9	1.6	0.096	6.1	0.41	25.6
fluoranthene	Extract B	11	11	21	1.5	7.0	5.3	25.4
	Extract C	11	9	2.7	0.14	5.0	0.85	31.6
benzo(e)-	Soil A	9	7	0.48	0.031	6.4	0.12	24.1
pyrene	Extract B	10	10	8.7	0.84	9.7	3.7	41.9
	Extract C	10	9	1.1	0.055	5.2	0.50	47.7
benzo(a)-	Soil A	11	10	0.66	0.040	6.1	0.18	27.4
pyrene	Extract B	12	12	10	1.1	10.3	3.2	31.1
	Extract C	12	8	1.2	0.064	5.2	0.28	22.5

VOC

Two soil samples (samples A and B), of two different levels of contamination, and one standard solution in methanol were prepared (Ringstad, 1997). The soil samples were sandy soil obtained from sites of polluted soil in Norway. The soil was air dried at room temperature. Coarse material was removed manually. The material was sieved through a 2 mm sieve and ground to an average size less than 500 µm. The organic content was 5.9% and 7.4% for samples A and B, respectively. No background levels of the target VOC compounds was detected in the blank soils. Aliquots of the soil was transferred to 40 ml vials with an open hole screw cap, and a Teflon coated septum. Water was added to the soil to represent 83% dry weight. The soil was spiked with test solutions containing the target compounds, and conserved with methanol before the vial with its content was sealed. The 11 target compounds included benzene, toluene, ethylbenzene, cumene, p-cymene, n-butylacetate, chlorobenzene, chloroform, 1,1,1-thrichloroethane, trichloroethene, and tetrachlorethene.

Each laboratory received 3 replicates of samples A and B together with one ampoule of the standard solution on May 1st and had to report their results before July 1st 1996.

11 laboratories submitted datasets, Denmark (4), Finland (5), and Sweden (2). No laboratories from Norway nor from Iceland participated. Eight of the laboratories used a solvent extraction method, while two of the laboratories used the Purge and Trap method. One of the laboratories participated with its own method only. The participants submitted full datasets with the exception of cumene, p-cymene and n-butylacetat, which some of the laboratories did not report.

The nominal concentrations of the VOC target compounds in the standard solution were used as assigned values. The grand mean was used as the assigned values for soil A and B. The results of the test are summarised in Table 6.

The test solution was reported with a reproducibility ranging from 15% (1,1,1-trichloroethane) to 40% (p-cymene). A similar range was observed for the soil samples. The results indicate that there were no significant differences in the performance of the standard solution compared with the soil samples. On the average 65% of the laboratories reported test results within ± 25% of the theoretical value. However, within the dataset, all laboratories had one or several values extending the ± 25 % level.

Table 6. The inter-laboratory test results for VOC.

Compound	Level j	N	pj	mj	S_r	CV_r	S_R	CV_R	Ref. val.
Benzene	1	11	10	3.07	0.30	9.8	0.76	24.9	3.5
	2	11	11	23.79	1.50	6.3	4.79	20.1	28.1
	Solution	10	6	7.25	0.20	2.8	2.35	32.4	8.8
Toluene	1	11	10	6.27	0.37	5.8	1.75	27.9	6.9
	2	11	11	22.58	1.42	6.3	5.39	23.9	24.3
	Solution	10	7	7.81	0.34	4.3	1.51	19.2	8.7
Ethylbenzene	1	11	11	5.74	0.36	6.9	1.95	34.0	5.5
	2	11	11	34.08	1.57	4.6	11.52	33.8	34.4
	Solution	10	7	8.49	0.38	4.5	1.68	19.8	8.6
Cumene	1	8	8	5.96	0.37	6.2	2.03	34.1	5.5
	2	0	0						ni
	Solution	7	4	8.03	0.27	3.4	1.29	16.0	8.6
p-Cymene	1	0	0						ni
	2	6	6	16.47	1.58	9.6	1.59	9.6	17.2
	Solution	5	3	10.34	0.72	6.9	4.20	40.7	8.6
n-Butylacetate	1	6	6	3.36	0.27	7.9	0.86	25.5	4.2
	2	6	6	14.53	0.48	3.3	3.41	23.5	17.6
	Solution	6	4	7.48	0.14	1.9	1.16	15.5	8.8
Chlorobenzene	1	11	11	3.06	0.18	5.7	0.77	25.0	3.5
	2	11	11	18.74	1.23	6.6	4.34	23.2	22.2
	Solution	10	7	10.08	0.42	4.2	2.11	21.0	11.1
Chloroform	1	11	11	3.65	0.32	8.7	1.42	38.8	4.6
	2	0	0						ni
	Solution	10	6	13.60	0.516	3.8	4.90	36.0	14.6
1.1.1-trichloro-ethane	1	11	10	5.50	0.57	10.4	2.04	37.1	7.4
	2	11	10	10.52	0.82	7.8	3.07	29.2	13.4
	Solution	10	6	11.63	0.23	2.0	1.78	15.3	13.4
Trichloroethene	1	0	0						ni
	2	11	11	13.99	0.90	6.5	4.73	33.8	17.5
	Solution	10	7	12.68	0.59	4.6	3.15	24.8	14.6
Tetrachloro-ethene	1	11	10	1.09	0.18	17.0	0.42	38.4	1.3
	2	11	11	24.85	2.05	8.3	7.71	31.0	32.4
	Solution	10	6	15.21	0.43	2.8	3.97	26.1	16.2

ni = not included

Most laboratories seemed to perform the analysis of nonhalogenated VOC's (benzene and alkylated benzene's) better than the haloforms. However, the number of participating laboratories was to low for the statistics to be conclusive. Only 6 of the participating laboratories reported test results for p-cymene and n-butylacetate, whereas 8 laboratories reported test results for cumene. One laboratory did not report results for the standard solution and three laboratories reported only single results for the standard solution.

The majority of the laboratories conducted the analysis within two weeks of receiving the sample set. One laboratory conducted the analysis after 7-8 weeks. Most of the reported values from the latter laboratory were within acceptable limits, but contained some extreme values. One laboratory conducted its own method only (static headspace). The reported standard solution results from this laboratory were good, but the results from the soil samples were only approximately 50 % of the theoretical values. This is consistent with observations

made by SINTEF, suggesting that a static headspace technique is not an appropriate method for quantitative analysis of VOC residues in soil.

PCB

The inter-laboratory test (Olafsdottir. 1997) concerned the analysis of 9 different PCB congeners (28. 52. 101. 105. 118. 138. 153. 156. 180) in one level of contaminated soil. Every laboratory tested the proposed Guideline method in three sub samples of the soil containing 0.3 g of CRM 481 from BCR mixed with 2.7 g of PCB-free soil and if desired their own method on a different set of the same soil. All laboratories were also supposed to analyse a solution that contained all nine PCBs to give an idea of the calibration and chromatographic performance. The analyte solution was made from neat crystals of respective congeners and PCB 31. from Promochem, Germany, and dissolved in isooctane p.a. The soil samples were sent out in screw-capped glass vials and the analyte solution in sealed glass-ampoules.

The samples were sent out on May 7, 1996. The number of laboratories receiving samples were 28 but only 21 returned results. Last date of accepted results was August 31, 1996. The results, which are summarised in table 7, revealed that many of the participating laboratories have problems concerning calibration of the individual PCB congeners and can therefore not be expected to give accurate results when analysing soil samples. It is evident that the preparation of calibrants and the method of calibration are a major source of error in the determination of PCBs. One of the 21 labs returning results did not analyse the analyte solution, but of the remaining 20 laboratories only 7-14 laboratories were able to determine the analyte solution within 25% deviation from the expected values.

Generally higher variability was found with the lower level congeners and it has been proposed by CEN to allow 100% variation at levels close to the detection limits of individual PCBs (around 0.01-0.05 mg/kg for the soil), 50% variation at a level 10x higher than that and 25% variation at still higher levels (prEN 1528-1:1996). Many laboratories did not analyse PCBs 105 and 156. These are usually present at low levels but are nevertheless very important congeners toxicologically (mono-ortho).

The treatment of PCB 138 was questionable, because it was unclear whether the laboratories were analysing 138 + 163 together, in which case the total amount detected would have been 12.3 instead of 9.2 for only PCB 138. The mean values were in-between these figures, so most laboratories were probably analysing the two together although they did not indicate that in their results and we therefore used 9.2 as the expected value.

14 laboratories tested their own method and in general not much difference was found between the Guideline method and the "own methods". Seven laboratories reported very good results, indicating that the method is sufficient for the purpose.

Table 7. The inter-laboratory test results for PCB

Congener	Level j	N	pj	Expected level	mj	Accuracy (%)	Sr	CVr	S_R	CV_R
28	A	17	11	0.03	0.032	107	0.007	21	0.022	69
	B	11	7	0.03	0.024	78	0.002	9.4	0.020	83
	Solution	18	18	32.2	47.1	146	2.6	5.5	18.3	39
52	A	20	15	0.29	0.28	97	0.01	5.0	0.10	35
	B	13	11	0.29	0.37	128	0.04	11	0.17	47
	Solution	20	18	29.1	28.5	98	1.9	6.7	6.9	24
101	A	21	21	3.7	3.5	95	0.19	5.6	0.95	27
	B	14	13	3.7	3.5	93	0.25	7.1	1.3	36
	Solution	20	20	45.7	44.8	98	1.9	4.2	9.9	22
105	A	10	7	0.1	0.37	373	0.017	4.6	0.38	102
	B	7	4	0.1	0.20	200	0.02	10.0	0.14	71
	Solution	12	10	20.2	20.6	102	0.92	4.5	3.9	19
118	A	20	16	0.94	1.18	126	0.11	9.6	0.80	68
	B	13	10	0.94	0.96	102	0.09	9.7	0.30	36
	Solution	19	17	33.8	29.4	87	0.97	3.3	8.1	28
138	A	21	21	9.2	11.1	121	0.78	7.0	3.8	34
	B	14	14	9.2	11.0	120	1.1	10	4.0	36
	Solution	20	18	131	119	91	3.9	3.3	33.6	28
153	A	21	20	13.7	12.5	91	0.66	5.3	3.9	31
	B	14	14	13.7	11.8	86	1.3	11	3.6	31
	Solution	20	19	71.4	69.0	97	2.3	3.4	19.8	29
156	A	12	10	0.7	0.83	118	0.05	6.4	0.29	36
	B	9	7	0.7	0.71	101	0.06	8.5	0.25	35
	Solution	12	10	62.2	58.6	94	1.9	3.3	4.6	7.9
180	A	21	21	12.4	11.8	95	0.82	6.9	3.7	31
	B	14	14	12.4	11.8	95	0.9	7.6	3.6	31
	Solution	20	16	74.1	70.6	95	1.9	2.7	16.0	23

CONCLUSION

The most crucial step in attaining a comparable analytical method, apart from the sampling, is the pre-treatment (i.e. crushing and sieving), the preparation step (i.e. extraction and digestion) and accurate and careful calibration of the instrument.

It is also important that the test report for organic compounds always contain a copy of the chromatograms from the analysis. In this way it can be seen which compounds are analysed and identified and the number of unidentified peaks. The water content of the sample should always be measured and reported, and the test results should normally be reported as mg/kg dry matter.

If the sample is sieved before analysis, this should be described in the report, and the weight of the two (or more) particle fractions from the sieving process should be reported. Only in this way is it possible to relate the concentration to the whole sample.

The inter-laboratory tests showed variable repeatability and reproducibility for the different methods, but this is more likely due to the lack of adequate quality routines in the

participating laboratories than to the method. In general, the Guideline methods had better reproducibility than the laboratories own methods. However, there is also room for improvements for some of the Guideline methods.

Heavy metals

The nominal concentration of the metals in the standard solution was used as the *assigned values*. The overall performance on the test solution was good with a total coefficient of variation CV_R between 3.73% for Cu to 13.9% for Hg. The laboratories seem to have larger difficulties analysing As and Hg than the other elements. The performance of the standard solution was regarded acceptable, although some poor results were reported.

The grand mean were used as the assigned values for soil A and B. For the soil samples the coefficient of variation CV_R varied between 6% to 26% for soil A and B, and between 6% to 40% for soil C. At least 75% of the participants were able to analyse the soil samples regarding Cd, Cr, Cu, Ni, Pb and Zn within 25% of the assigned values, but only between 60 and 75% were able to analyse As and Hg within 25% of assigned values, respectively. The testing of homogeneity of the test samples showed a variation which was less than 5%.

Soil C was certified for all the elements of interest except for Pb. It was revealed during the test that this soil sample was not completely homogeneous and gave a higher coefficient of variation CV_R than soil A and B.

The proposed method for analysing heavy metals in contaminated soil seems to work sufficient for its purpose. All datasets contained extreme values, and indicate that some of the participating laboratories need to improve their quality assurance.

Chlorophenols

The test material was field moist, obtained from a contaminated site, representing a relevant composition of soil and sawdust. Homogeneity experiments revealed a variation of 2-22%, which was deemed acceptable for this kind of samples. The repeatability variation coefficient, CV_r, which indicates the within-laboratory variation was also satisfactory. It was lower than 8.1% for the test solution and less than 17% for all the soil samples. The results of the inter-laboratory test showed, however. that the reproducibility between the laboratories to analyse the chlorophenol solution was very poor. The coefficient of variation, CV_R, for the solution ranged from 17.3% to 34.1% and for the soil samples from 31.8% to 71.1%.

The variation may be due to the fact that the laboratories used the tested method for the first time and thus had problems finding the right level of concentration. However, this problem can be overcome by better validation in separate laboratories. At present there is no commercial reference material available. The reason for the variation in the results for the soil samples, however, was not due to the quality of the test material, but rather due to problems with the analytical performance, as was evident from the results for the standard solution. The CV_R was highest for soil C, which had a very high concentration. For soils A and B it varied from 31.8% to 47.9%.

Creosote

The within laboratory variation was quite acceptable, although there is room for improvement especially for the soil sample. The between laboratory variation was quite large, probably due

to a number of reasons. For instance, the 60% variation for naphthalene in the soil sample is likely explained by evaporative losses being controlled to a varying degree among the laboratories.

The within laboratory variation for the 21 compounds was:

Sample A, between 4.0% (for biphenyl) and 21% (for naphthalene).
Sample B, between 1.4% (for fluorene) and 11% (for carbazole).
Sample C, between 2.3% (for acenaphthene) and 6.2% (for p-cresol).

The between laboratory variation was:

Sample A, between 17% (for dibenzofuran) and 60% (for naphthalene).
Sample B, between 8.4% (for 2-methylnaphthalene) and 42% (for benzo(e)pyrene).
Sample C, between 6.3% (for dibenzofuran) and 48% (for benzo(e)pyrene).

The results from the methods evaluation showed that the method is a good candidate for recommendation on a Nordic basis. It should however be pointed out that a less contaminated soil probably requires a more specific method, e.g. gas chromatography in combination with mass spectrometry (GC-MS). Also, it should be kept in mind that soil samples of different origin may have substantially different properties, and that the soil used in this investigation should not be regarded as being representative for the majority of contaminated soils. There may very well be other soil types, e.g. with higher humic content that would yield less favourable results as far as the method evaluation is concerned.

VOC

The overall reproducibility was considered to be acceptable, but there is room for improvement. The results suggest that some of the observed differences are related to factors within the laboratories, and are not related to obvious weaknesses in the proposed method. A strong indication of this is the fact that the reproducibility results of the test solution were comparable with the results of the soil samples.

The test solution was reported with a reproducibility ranging from 15% (1,1,1-trichloroethane) to 40% (p-cymene). A similar range was observed for the soil samples. Most laboratories were able to analyse the samples within ± 25 % of the theoretical values. Some extreme values were observed, but can probably related to errors in the analytical performance of the laboratory in question rather than to limitations in the proposed method. The proposed Guideline method includes some critical steps which, when handled improperly, can give erratic analytical results. One is the proper handling of the VOA vial when extractant solvent is added to the soil/methanol phase.

The soil/methanol phase should be mixed well in the sealed vial prior to the addition of extractant solvent. It is recommended to add the extractant and the internal standard solution directly into the sealed vial. Opening of the vial first may result in losses of VOC's. The second critical step is the calibration. Standards for calibration should be freshly prepared. Stock standards must to be controlled and preferably renewed every 3 months. Keeping control of the critical steps above, most VOC's can be quantitatively analysed with the proposed Guideline method.

PCB

After the exclusion of outliers the reproducibility (CVR) for the analyte solution ranged from 8-29%, except for PCB 28 where the reproducibility was only 39%, most likely because some laboratories were not separating PCBs 28 and 31 adequately. For the soil, reproducibility was dependent on the level found, so that when close to the detection limit it was close to 100%. but when levels were higher, the reproducibility improved to about 30% except for PCB 118 with only 68% reproducibility, possibly due to insufficient separation from PCB 149.

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EFFECTS OF REDOX POTENTIAL ON NATURAL ORGANIC MATTER: FIRST RESULTS FROM FLOW-FFF-MULTI-DETECTOR ANALYSIS (4F-MDA)

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Key words: Flow-Field-Flow-Fractionation, hydro-colloids, soil, humic acids, redox conditions, laser light scattering, fluorescence detection

SUMMARY
A design for a flow-field-flow-fractionation with UV/VIS-, fluorescence- and laser-light-scattering-detectors is presented. Extracts from a humus rich horizon of a gleyic podzol are characterised for their molecular weight distribution. Main objective is the investigation of colloid alteration during processes provoked by main geochemical driving forces (e.g. redox-ptential, pH or ionic strength).
It could be shown that the conditions of the surrounding medium alter and control the size-distribution of dissolved natural organic substance (DNOM) and spectral data give evidence for differences in the inner structure dependent of the size region of mostly aggregated DNOM. Size distributions found for natural samples differ from those reported for pretreated standard NOM in the order of magnitudes.

KURZFASSUNG
Ein Flow-Field-Flow-Fractionation System mit Mehrfachdetektion (UV/VIS-, Fluoreszenz- und Mehrwinkel-Laser-Streulichtdetektor) wird beschrieben. NOM-Extrakte eines Gleypodsols wurden auf ihre Molekülmassenverteilung charakterisiert. Zentraler Aspekt der Studie ist die Frage inwiefern geochemische Gradienten (Redoxpotential, pH-Wert, Ionenstärke) die Molekülgrößenverteilung von DNOM verändern bzw. kontrollieren.
Es konnte gezeigt werden, daß die Begleitsubstanzen in einer unveränderten natürlichen Probe die Erscheinungsform der DNOM maßgeblich beeinflussen. Auswertungen der spektralen Daten weisen auf Unterschiede in der Struktur der DNOM-Aggregate hin. Molekülmassenverteilungen der untersuchten DNOM unterscheiden sich um Größenordnungen von denen die für erwerbliche, vorbehandelte Standardhuminstoffe veröffentlicht wurden.

Contaminated Soil '98, Thomas Telford, London, 1998, 279–288

INTRODUCTION

Transport processes in the subsurface are often described using a two phase model: a solid, immobile phase and a mobile aqueous phase. Nonpolar organic contaminants bind to natural organic matter (NOM) and inorganic micropollutants, like heavy metals or radioisotopes, tend to sorb strongly to mineral components of the aquifer matrix. Both are supposed to be retarded compared to the groundwater flow. These pollutants seem to be only virtually immobile because transport in the subsurface may also occur in the form of micropollutant associates with colloidal matter. The colloidal phase, often defined as particles between 0.001µm and 1µm, can play a major role due to its high specific surface area and high mobility. The importance of this fraction was pronounced within the last two decades. McCarthy and Zachara, (1989); Buffle and van Leuween, (1993), Buffle and Leppard, (1995), and Ouyang et al, (1996) gave comprehensive overviews.

The fate and transport potential of colloids as carriers of pollutants is closely related to the conditions of the surrounding medium. In subsurface environments one of the forces altering the composition of colloid suspensions or the colloid itself are geochemical gradients. These gradients are produced by changing redox potentials due to organic substances available for biogenic degradation or oxygen delivery from the vadoze zone (Christensen et.al, 1994). These changes in redox potentials can cause the dissolution of iron and manganese oxides followed by the release of pollutants bound to the surfaces, disaggregation of clay aggregates or iron-oxide-humus clusters, both leading to smaller, more mobile particles. On the other hand re-oxidation of anoxic groundwater can result in precipitation of hydrous iron/manganese oxides followed by adsorption of pollutants to the surface of these particles. Dependent on the solution chemistry, aggregation of these precipitates may occur with subsequent filtration or immobilisation of aggregates.
This work focuses on dissolved natural organic matter (DNOM), because of their immanent complexing capacity for many heavy metals and radionuclides and because of the dominant adsorption of hydrophobic organic contaminants (e.g. PAH) to their structure. Additionally the „diameters" of DNOM are in the low nanometer region, responsible for fast migration in the subsurface environment (Enfield & Bengtsson 1988).

Separation and characterisation of particles with respect to their variation under changing physical/chemical conditions is an appropriate approach to study the impact of these redox processes to the constitution of DNOM. Separation can be done by fractionating centrifugation (Peret et al, 1994; Angehrn-Bettinazzi, 1989), sequential ultrafiltration or gel-permeation-chromatography, in particular for DNOM (DeNobili et al, 1989). Another promising approach is the very low invasive, broad applicable field-flow-fractionation (FFF) (Barth & Flippen, 1995). Flow-field-flow-fractionation (4F), as a subtechnique of FFF, is able to separate particles between 1nm and 1µm in normal mode, according to their diameter or diffusion coefficients (Fig. 1). Particle size is calculated from retention times via basic FFF-theory or by calibration with standards of known size or molecular weight. Theory of 4F and applications to environmental particles are widely described (Beckett, Zhang and Giddings, 1989; Beckett and Hart, 1993; Dycus et al, 1995 and Moon, 1995). In FFF size distribution data of natural

samples are usually acquired by online UV/VIS-detectors coupled to the outlet of the FFF-channel. Other techniques are reported, e.g. coupling to ICP-MS (Murphy et al, 1993). Since lifetime of colloidal suspensions can be very short and alterations of the analyte may occur while collecting fractions and subsequent analysis, it is of importance to acquire relevant data online.

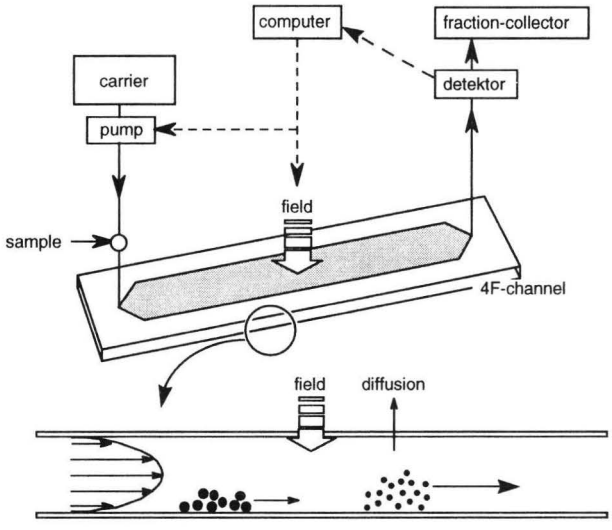

Fig. 1: Schematic plot of FFF system-layout and basic principles of particle fractionation. Against the external field (rectangular cross-flow) and according to their larger diffusion coefficients, smaller particles are focused in regions of larger carrier-flow vectors and elute before the larger particles.

UV/VIS-detectors are appropriate and provide good sensitivity for detection of DNOM because of the specific absorption of aromatic and unsaturated structures at wavelengths around 250nm. Information about aromaticity can be retrieved from spectra provided by diode-array detectors or with multiple runs at different wavelengths.

Fluorescence detectors, especially by scanning fluorescence spectra, can provide additional information about analyte composition that is neglected by UV/VIS-detection (Müller-Wegner, 1976; Paolini, 1978; Huber, Gremm & Frimmel, 1990 and Ziechmann, 1994).

Multi-angle-laser-light-scattering (MALLS) detectors provide information about particle size and/or molecular weight from the light scatter intensities measured simultaneously at different angles to the laser light source and carrier stream. The use of MALLS is not common with environmental samples, but coupling with 4F for macromolecule characterisation is reported by Thielking & Kulicke (1996).

METHODS

Samples. For all experiments cold water extracts from the Ah-horizon of a gleyic podzol near Neumunster, Northern Germany were used. The soil was air-dried and sieved to

<125µm. Extraction was performed in the dark with deionized water in 1,000mL Duran-glasware bottles. Every day the bottles were shaken for 30 seconds. The solid/liquid ratio was 1/10. Oxic and anoxic conditions were provided by purging with air and argon respectively. The development of redox conditions was monitored by regular sampling and measurements of redox potential and pH.

sample	conditions	pretreatment
AN1	natural pH=4,3; 1g/L glucose added	24h settled prior injection
OX1	natural pH=4,3; 1g/L glucose added	24h settled prior injection
AN2-4	adjusted pH=4,0	centrifuged 20min at 4000rpm
AN2-7	adjusted pH=7,0	centrifuged 20min at 4000rpm
OX2-4	adjusted pH=4,0; 7 days reoxidised AN2-4	centrifuged 20min at 4000rpm
OX2-7	adjusted pH=7,0; 7 days reoxidised AN2-7	centrifuged 20min at 4000rpm

Tab. 1: Samples used in this study

Flow-Field-Flow-Fractionation (4F). The fractionation system is equipped with a Model F-1000 channel from FFFractionation Ltd, a Hewlett-Packard HP 1100 isocratic HPLC pump for the carrier, and a Pharmacia LKB-P500 syringe pump in a closed circuit for the cross flow field. A Waters LambdaMax 481 spectrometer was used as online UV/VIS-detector and for online fluorescence detection a Shimadzu RF 535 Fluorescence HPLC detector for static single wavelength measurements and a Gynkotech RF1002 HPLC fluorescence monitor for spectrum-measurements. Light scattering data are online retrieved from a MALLS (multi angle laser light scattering detector) MiniDAWN™ from Wyatt Technologies. Carrier solution consisted of 0.05% sodium-dodecylsulfate (SDS) and 0.02% sodiumazide in water (Moon, 1995).

4F-field-programming. By using a constant field, the relatively high crossflow-rates, that are needed for separation of humic substances in the lower molecular weight range, would increase the elution time for aggregates and small mineral components, leading also to extensively peak broadening and loss of sensitivity. (Williams & Giddings, 1994) The applied field-programming obtains a size range up to 150nm within 40 minutes. The field-programming is performed by runtime controlled variations of the cross-flow. Parameters are listed in table 2.

	start		start	**gradient**	end	**stop**	
	mL/min	runtime	mL/min	runtime	mL/min	mL/min	tot. runtime
Samples „1“	3.0	3.5 min	3.0	6.5 min	0.35	0.35	40 min
Samples „2“	5.0	5.0 min	5.0	20 min	0.20	0.20	40 min

Tab. 2: Parameters for the cross-flow field-programming. Carrier flowrates where 0.5mL/min in both cases.

For evaluation of particle size measurements of the MALLS detector, DUKE Scientific polystyrene-latex-beads were used (50nm and 220nm certified diameter). For the

transformation of retention volumes to molecular weight four polystyrene-sulfonate molecular weight standards were used.

RESULTS AND DISCUSSION

Regarding the samples OX 1 and AN 1, it can be seen easily from the UV-VIS (254nm) fractogramms that there is an significant difference in molecular weight distribution (Fig. 2). Two different regions of size or weight are recognised together with a transient plateau between the void region (0-2mL elution volume) and first sample peak.

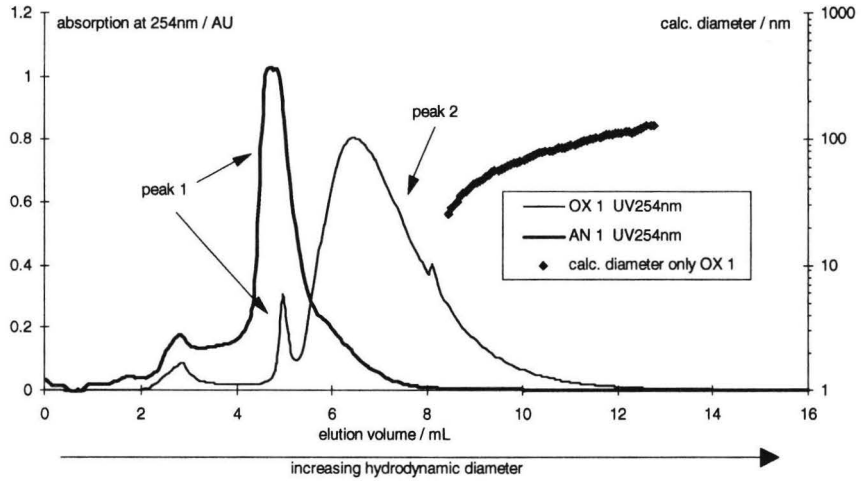

Fig. 2: Comparison of the oxic and anoxic extract from a humus-enriched soil. 4F-UV/VIS (254nm) fractograms are shown. The calculated particle diameters are retrieved by MALLS only from the oxic extract.

The anoxic extract AN 1 gives only one peak in the region of small molecules, while the oxic extract OX 1 shows two peaks, peak 1 with almost the same elution volume as peak1 in the anoxic sample and a second (peak 2) in the region <10nm to around 100nm diameter.

The MALLS-calculated diameters for the oxic sample are in good accordance to the elution volume of 50nm-latex-beads (50nm OX 1: 9.23mL and latex-beads 50nm: 9.16mL). MALLS-detection fails for sample AN 1, diameter calculation is only possible above 20nm particle diameter.

λ	OX 1 (total)	AN 1 (total)	OX 1 (peak1)	AN 1 (peak1)	OX 1 (peak2)
254nm / 350nm	5.10	4.55	4.5	7.5	5.1
254nm / 450nm	13.38	35.25	9	40	12.44

Tab. 3: Comparison of peak area data retrieved by multiple runs at different detection wavelengths.

Regarding the UV-absorbance peak data as well as signal ratios of different detection wavelengths (Tab. 3), there is evidence that, beside the different elution schemes,

DNOM extracted from the same soil differs in structure, depending on the solution conditions. Since a chemical alteration of the DNOM molecules itself is implausible, the observed variation in absorbance properties seem to be related to different stages of agglomeration of the DNOM.

Fluorescence fractograms support this assumption (v.d.Kammer & Förstner 1998). Basic differences between the size regions can be shown with static fluorescence detection at different excitation-emission wavelengths (Fig. 3).

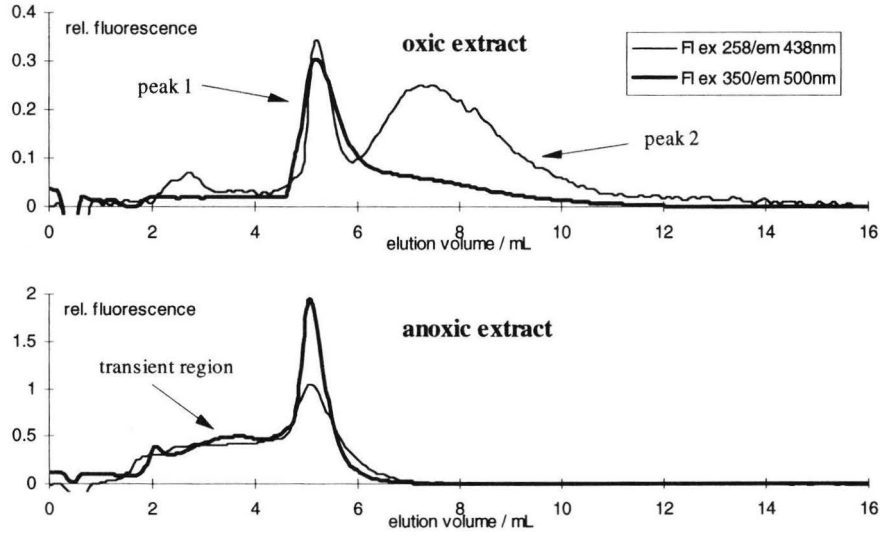

Fig. 3: 4F-fluorescence-fractograms at different excitation/emission pairs. The 350nm/500nm pair produces nearly no response for the second oxic peak, for peak 1 the signal ratios differ significantly for anoxic and oxic sample.

Larger DNOM aggregates produce a selective quenching of the intrinsic fluorescence at the ex350/em500nm pair. Excitation at 350nm and detection at around 500nm was used by Green et al (1992) for studies of the electrostatic properties of DNOM by fluorescence quenching. The 258/438nm-pair was used for DNOM size distribution measurements by Huber et al (1990). Since metal-DNOM interactions can alter the fluorescence properties of DNOM (Cabaniss 1992) it is likely to assume, that one or more of the main redox sensitive metal constituents (Fe or Mn) of the solution are at least partially responsible for the observed agglomeration and fluorescence quenching effect.

To investigate the pH dependence of the observed DNOM variations and to exclude interferences caused by the glucose addition to the batch extracts, two batches were prepared and stabilised at pH4 and pH7 by addition of diluted nitric acid and sodium hydroxide respectively. Both extracts became anoxic over 90 days with no significant deviation in redox potential (+20mV, corrected for pH7). Subsamples were reoxidised by air purging over 7 days. Redox conditions and the actual pH control the size distribution of DNOM (Fig. 4).

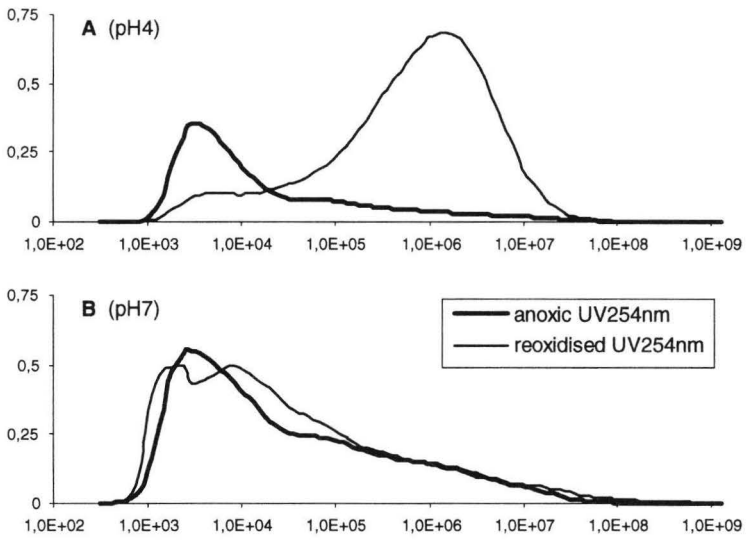

Fig. 4: Comparison of UV/VIS-fractograms of DNOM extracted at pH4 and pH7. Extracts were held anoxic and subsamples were reoxidised for 7 days. UV-absorbance is plotted against molecular weight (in Dalton).

NOM, especially humic acids are known to be more water soluble at higher pH values mainly because of deprotonation of carboxylic groups. Additionally the dissolved molecules are stabilised at low molecular weight aggregates or single molecules, almost independent of redox conditions. At lower pH values aggregation due to oxidation of the solute is much more pronounced. Peak areas are increasing as was observed for OX 1 (Fig. 2).

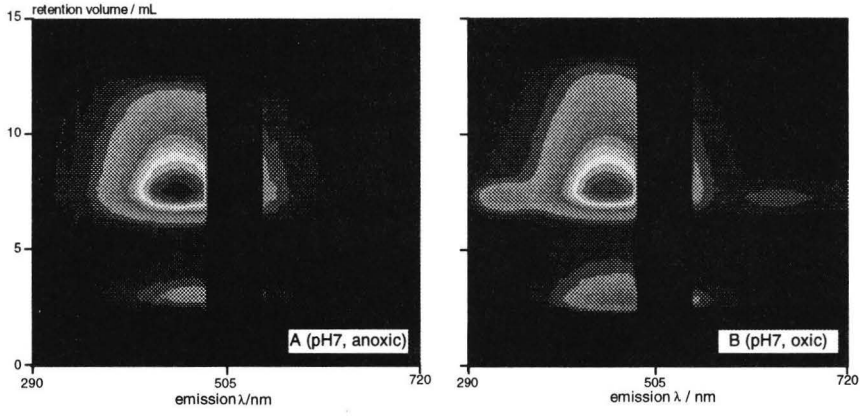

Fig. 5: 3D-contour plots of the fluorescence-spectrum-fractograms. Excitation at 250nm, relative fluorescence intensities are: black=low, grey to white=increasing, white to grey in peak region=highest. The black bar between 480nm and 530nm is related to the second order emission from the excitation monochromator. Data in this region were eliminated to zero by subtraction of baseline-spectrum.

To yield more information about the properties of the DNOM than retrieved from single wavelength fluorescence measurements, flourescence-emission spectra were taken on-line throughout the fractionation run. Figure 5 shows the results in 3D-contour plots for sample AN 2-7 and OX 2-7. The related UV/VIS-data are given in Figure 4B. It has to be stated, that overall fluorescence intensities for the sample AN 2-4 and OX 2-4 (pH4) were only about 25% of the intensities observed in the pH7-samples.
Spectrum measurements show a broadening of the fluorescence emission spectrum in the oxic extract in a isolated region of 7.4mL elution volume (corresponding ca. 100 kDa molecular weight). This effect is not easily to explain. It occurs to a minor extent also in the oxic pH4-extract and may be related to an increase of fluophore types in the DNOM structure. Beside this, the similarity of the fluorescence-spectrum-fractograms, especially regarding the differences in UV-fractograms, shows that more than the considered effects are present. The application of synchron spectrum acquisition could give more information about this.

CONCLUSIONS

It could be shown that the conditions of the surrounding medium alter and control the size-distribution of dissolved natural organic substance (DNOM). Formation of DNOM with high molecular weight in the 10^6 Da-region is observed under oxic conditions. It seems to be obvious that these molecules consist of aggregates of smaller primary units. Low pH conditions support the aggregation during reoxidation of an anoxic extract. Under neutral conditions the size distribution of DNOM is stabilised in the 10^4 Da-region and almost independent of redox conditions within the observed period of time.
Spectral data give evidence for differences in the inner structure dependent of the size region of mostly aggregated DNOM.

The molecular weight distributions observed with 4F are in the order of magnitudes greater than reported for humic acids available as standard materials by Beckett (1993) or Dycus (1995). The pre-treatment steps for these substances seem to reduce the observed molecular weight to the primary molecule weights. This study could show that in untreated almost natural samples the distribution of DNOM is dominantly controlled by the solution chemistry and that primary molecule sizes seem to play a minor role in natural systems.

Fluorescence-data support the assumption of aggregate forming under natural conditions. Aquisition of fluorescence-emission-spectra, on-line during the 4F-run, give additional information which is not easily to explain at this status of the study.

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Theme D:
Risk assessment, quality and health criteria

DEVELOPMENTS OF RISK ASSESSMENT AND RISK MANAGEMENT

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Key words: Environmental policy instruments, environmental risks, guidelines, health risks, psychosocial aspects, ranking systems, risk, risk assessment, risk management, trigger values.

SUMMARY

Risk assessment and risk management of contaminated sites is starting to become current practice in most industrialized countries. Until now risk assessment has mostly been used to assess the need for soil remediation and to set priorities in clean up programs. There is less experience with the development of risk based clean up goals and risk based management of contaminated land. For the development of appropriate risk assessment methods a major research effort will be needed to overcome the limitations of the present methods. This is generally recognized. Implementation of risk assessment methods within an environmental policy and decision making framework may also critically depend on the competence and expertise of local authorities and industrial risk managers. The paper will review the more important methodological issues in the current risk assessment approaches and make some suggestions to improve their implementation.

Contaminated Soil '98, Thomas Telford, London, 1998, 291–299

INTRODUCTION

The use of "risk assessment" in environmental policy probably originated in the USA. The first aim of risk assessment was to set priorities for environmental protection in an objective and scientific way, avoiding political "perceptions" of the administration. According to the National Academy of Sciences (1983) the procedure should separate risk assessment (the objective scientific part) from risk management (the policy driven decisions about risks). In practice however risk assessment cannot be strictly separated from risk management, because specific management problems may determine the way an assessment has to be carried out.

Although "Risk" is becoming a central concept in environmental policies, this does not mean that risk is an easy and well defined concept (Vlek 1995). There is an ongoing scientific debate about the measurability or predictability of risk between statisticians and technological risk assessors on the one hand and social scientists and psychologists on the other hand.

Risk assessment as a tool is not limited to the assessment of contaminated land. It is mostly used for other purposes varying from prevention of pollution from new chemicals and pesticides, industrial activities and new technologies and environmental impact assessment. In contaminated land problems risk assessment methodology has up till now mainly been used to set priorities, which means that risks are not used as an absolute quantitative measure describing the environmental or human health impact of soil contamination but as an indicator that is used for comparative purposes only. A better term for risk based priority setting is "comparative risk analysis". "Risk assessment" is the scientific description about the informal question about "how risky a situation is".

Risk assessment of contaminated sites is somewhat different from risk assessment in other fields. The evaluation of the risk of soil contamination is not a preventive approach. Unlike in the other fields the source is already there. This makes the assessment easier in principle because claims about exposure and risks can be verified at the site. In practice however this advantage is rather limited due to the complexity of the soil environment and difficulties in performing experiments. If solutions to soil problems (clean up goals) involve risk considerations, a predictive risk assessment must be performed, which has more in common with risk assessment methods used in other fields.

A GENERAL FRAMEWORK

Contaminated land risk assessment generally considers the following endpoints:

- Human health: ADI (Acceptable Daily Intake), TDI (Tolerable Daily Intake) and cancer risk levels are used to quantify this endpoint.
- Ecological risk: is at present mostly quantified on the basis of laboratory toxicity experiments.
- Groundwater risk: this risk is related to the dispersion of pollution in groundwater.
- Construction: effects of soil pollution on structures and construction works.

Risk assessment of contaminated land usually starts with some suspicion about the presence of soil pollution. Results may be compared with generic soil and groundwater criteria or can be evaluated using models to predict adverse effect of pollution and the need for remediation. These model conclusions can be substantiated by actual measurements of exposure or even epidemiological data. In general the less prediction the more reliable is the assessment, but the more difficult is the investigation.

A general overview of risk assessment, from preliminary investigations to conclusions about risks and communication is illustrated in figure 1. Although risk perception and communication is located at the end of the assessment process in figure 1, it must be stressed that perception may already influence decision making as soon as preliminary investigations suggest that the site of concern is suspect. The strength of the risk assessment methodology is to keep decision making as objective and transparent as possible, in order to prevent politicization due to different perceptions and interests of the parties involved.

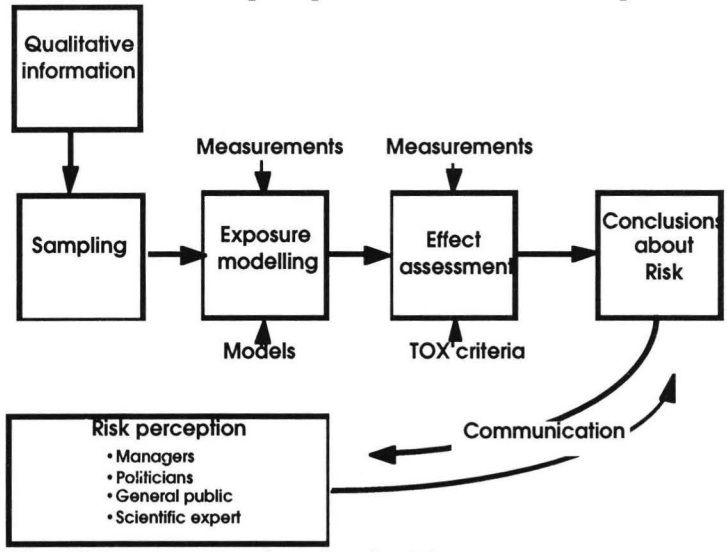

Figure 1 The different steps to be taken in risk assessment.

Mathematical models are an important part in risk assessment procedures. They are mostly used to predict exposure on the basis of the results of chemical analyses in soil and groundwater. A comparison with acceptable daily intake may then be used as a measure of "human health risk".

If risks are predicted from chemical analysis of soil and groundwater samples the models are run in forward mode. If local conditions are used to calibrate the models, they are applied in a procedure generally called "site specific risk assessment". Generic risk assessment on the other hand will mostly be performed by comparing concentrations of contaminants in soil and groundwater with generic guideline values, trigger values or soil screening values. These terms do very often mean the same: a normative value for a concentration of a contaminant in soil or groundwater that is used as a yardstick for preliminary assessment of soil pollution. In a risk based approach they are typically the result of the use of models in reverse mode. Based on a given risk level (or level for acceptable daily intake), a concentration of the contaminant in soil and groundwater is computed that corresponds with the risk level.

Risk assessment is, if properly performed, an objective way of assessing the potential impact of soil pollution on human health, ecosystems and the environment in general. A complete risk assessment is however a very detailed investigation of all sources, pathways and targets of concern at a given site. This is a tedious and costly procedure. Therefore a preliminary screening of a suspect site is very expedient (Siegrist 1990), expensive risk assessments are restricted to those sites that may impose real risks and where decisions about clean up are difficult due to the complexity of the site and/or the costs of the remediation. Most countries nowadays advocate a tiered or stepwise approach in contaminated land risk assessment and similar views are held by the industry as shown in the recent "European oil industry guideline for risk-based assessment of contaminated sites" (CONCAWE, 1997). Trigger values, guideline values or soil screening values are used for preliminary assessment or to facilitate "rule of thumb" decisions about clean ups for smaller sites where a full blown risk assessment would lead to disproportional costs.

IMPROVEMENT OF CONTAMINATED LAND RISK ASSESSMENT

It is beyond the scope of this paper to review all open problems in current contaminated land risk assessment. Two concerted actions funded by the EU, CARACAS (Concerted Action on Risk Assessment for ContAminated Sites in the European Union) and NICOLE (Network for Industrially Contaminated Land in Europe) have recently identified a large number of research needs (CARACAS & NICOLE 1997). Research will be needed in scientific disciplines concerning the various building blocks of risk assessment, such as behaviour and biological availability of soil contamination, ecotoxicology and

human toxicology, but also for the development of integrated assessment approaches and their implementation. Lack of integration of the various components of risk assessment and the relation between risk assessment and policy issues may be considered as a major weaknesses in the current approaches. The following issues will be discussed:

- Integration of soil sampling, exposure modeling and toxicological endpoints.
- Management of uncertainties.
- Perception of risk and communication.

Integration

Current risk assessment is still based on results of scientific research done for other purposes. Contaminated land risk assessment is not yet a scientific discipline. Whether current contaminated land risk assessment really answers the question of "risk" or the question of "fitness for use", which is the cleanup objective in most countries, may still be questioned.

"Fitness for use" is a broad concept which may be related to a large number of soil quality requirements. Current toxicological endpoints used in risk assessment may not be sufficient to assess fitness for use. The following may serve as an example. Ecological risks are often only associated with risks of pollution for nature. However, many forms of landuse by man do need a certain level of ecological functioning in soils, sometimes referred to as life support system. In the derivation of land use based clean up goals discussions about human toxicology dominate and the requirements of the life support system are mostly neglected.

Integration is of utmost importance if risk assessment is to be more than a mere sequencing of separate disciplines like soil sampling, exposure modeling and (eco)toxicology. In a fully integrated approach choices of toxicological endpoints must have consequences for the design of soil sampling schemes and exposure models and vice versa. Human health risks, ecological risks and groundwater risks should be specified in space and time in view of the spatial resolution of soil investigations and the time frame of the assessment.

Integration of the various components in risk assessment must be stimulated by the administration and larger industries by stressing the importance of sound risk assessment methods and by providing funds for special research and development programs. It is doubtful whether contaminated land risk assessment will emerge as an integrated scientific discipline on it's own through an autonomous development in already existing scientific disciplines.

Risk assessment and the management of uncertainties

The scientific definition of risk as "a combination of the consequence of a negative effect and the probability of that effect to occur", and the often large uncertainties in risk estimation both encourage the use of statistical approaches and the application of decision rules based on the amount of uncertainty. Current risk assessment procedures in most countries lack a statistical basis and do not assess the uncertainties associated with the result of an assessment. Recent developments in the USA and UK (Ferguson, and Denner, 1993) have shown that such an approach is feasible. An analysis of the uncertainties of an assessment may lead to more extensive and costly investigations. On the other hand it seems a waste of money to perform a detailed investigation in situations where conclusions are already clear after a preliminary investigation, just because of the protocol. Taking uncertainties into account may lead to lower costs in this case. Parties that are responsible for the site (landowners, practitioners) may have a choice here. They could decide to spend more money to increase their level of confidence, even if the conclusions seemed clear at the preliminary investigation stage.

Sound risk management decisions must take the uncertainties in risk assessment into account. The structure of models, statistical considerations and the choice of appropriate decision rules may contribute to uncertainties. The framing of the policy question underlying the assessment is however of prime importance for the role of uncertainties in decision making. Shrader frechette (1996) suggested a number of rules to cope with uncertainties in risk assessments. Whether a certain risk is acceptable is not a scientific question. Scientists can only assess the likelihood of occurrence of an adverse effect. However if they act according to the scientific tradition that there is no effect unless it is proven beyond all statistical doubt, risk management will not be very protective. Lack of information seems to promote safety in this case. Scientists involved in risk assessment must therefore avoid false positive conclusions about risk as well as false negative ones. Risk assessment needs a "three valued frame": negligible risk - risk cannot be proved to be absent or present - risk is present beyond reasonable doubt.

The considerations described above may lead to the following rationale in risk assessment for contaminated sites:

Risk assessment of contaminated sites can be used in two ways:
To describe the risks at a given site in order to establish the necessity and the priority of a cleanup, and to set generic or site specific clean up goals and to predict residual risks after (partial) clean up. It is well appreciated that risk assessment is subject to large uncertainties especially when modeling is used. Uncertainties can be reduced if models can be verified and refined by additional

measurements. This is possible in a present situation, but for the prediction of future situations one has to live with the large uncertainties associated with the model. In principle if risk assessment is used to derive clean up goals, larger safety factors should be applied.

The perception of risk

Risk perception may be governed by a number of factors (Vlek 1995), but the main difference with risks estimated by formal scientific methods is that risk is perceived more intuitively. Risks related to adverse effects that are conspicuous, known from experience, occurred recently or in the immediate surroundings are often overestimated.

Apart from bias in our capacity to assess certain risks the assessment is also influenced by so called "affective factors". Some people are more optimistic than others. People are also not likely to change their opinions about risk. Perception is persistent. In general people find the probability of an event less important than what will actually happen. This is important for the acceptance of the risk (Uijtdewilligen *et al* 1992).

The factors influencing risk perception and acceptance are important for communication of results of formal risk assessment to the general public. Effective communication does not exclusively depend on the perception of the public but also on the characteristics of the communicator, the message and the medium that is used. Specific guidance on how to communicate risks of contaminated land is lacking in current contaminated land risk assessment procedures. Communication is very important because risk assessment may require the acceptance of the procedure and the results among all parties involved. It is beyond the scope of this paper to give a full treatment on risk communication. One final suggestion is that it may be easier to communicate about soil quality (this piece of land is still fit for ..... And will be fit for..... After clean up) than to communicate about risk (there is still pollution left but the authorities state that your risk is acceptable). From a communication point of view it might be better to frame clean up goals in terms of soil quality or fitness for use instead of in terms of risk.

NEEDS FOR PRACTICAL IMPLEMENTATION

Improvement of risk assessment for contaminated sites is not only dependent on fulfillment of the research needs identified by NICOLE and CARACAS. Other requirements have to be met, the most important ones are:

- Training of risk assessors and decision makers
- Network for communication of new approaches and practical experiences
- Linking science to real world problems

Training of risk assessors and decision makers

The science behind risk assessment has to be applied in a local decision making context. Which means that local decision makers must have the expertise to handle the science or to have the expertise to control hired consultants performing state of the art risk assessment. In most countries there is a large need for training the local contaminated land risk managers which make decisions about individual sites. This is especially needed in view of the variability in soil conditions, the many uncertainties and other methodological pitfalls in the current risk assessment approaches and soil screening values.

Risk assessment only leads to a right decision if the limitations of risk assessment are recognized. Sometimes the risk assessment cannot provide all the answers and "risky decisions" will have to be taken. This is not new in environmental policy at least at the national level. However the numerous cases of local soil pollution will ask for this type of decision by local authorities which may not be very competent in these matters.

Network for communication of new approaches and practical experiences

After training, people have to maintain their expertise. They will also gain practical experience with various forms of risk assessment in different situations. These experiences are also of interest for others. The perspectives of safe solutions for contaminated land problems are larger if they are based on common knowledge and do not critically depend on an individual assessor. Most countries will need a platform for discussion to preserve current experiences for the future, for the dissemination of new approaches and to determine research priorities.

In view of the many scientific questions in risk assessment and the fact that present day science is performed in an international context, an international network for the scientific aspects of contaminated land risk assessment must also be formed and maintained:

- To avoid unnecessary duplication.
- To provide a basis for scientific peer reviews.
- To provide a common database for toxicological and other basic data.
- To promote international cooperation on the assessment of toxicity and carcinogeneity of substances.
- To promote mutual understanding of the way science is put to work in national policies.

The current concerted actions NICOLE, CARACAS and CLARINET (Contaminated land rehabilitation network) may serve as starting points for such a network.

Linking science to real world problems

Traditional fundamental science aims at establishing general theories that are tested against observations under controlled and defined circumstances. Very often theories cannot be directly applied in complex areas like soils and ecosystems. A long period of applied research is needed before some products of fundamental science can be made useful in real world problems such as the assessment of risks of contaminated land.

A more promising strategy is not to wait till contaminated land catches the attention of the fundamental scientist and the products of the fundamental scientist catches the attention of the applied scientist, but to bring all sorts of scientist to real world soil problems. The solutions generated may be less fundamental and universal than products of fundamental sciences, but they may be applied directly. Generalities and scientific theory may evolve as practical experiences with contaminated land problem solving accumulate. A close linking of fundamental and applied research programs to concrete contaminated land problems may be the best way to improve current contaminated land risk assessment.

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THE UMS-SYSTEM FOR EXPOSURE AND RISK ASSESSMENT OF CONTAMINATED SITES

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Key words: contaminated sites, exposure model, human-health risks

SUMMARY
For the detail assessment of abandoned contaminated sites the UMS-system was developed to calculate the kind and extent of exposure for human health and groundwater targets. The methodical concept of the UMS-system - assessing the actual or potential exposure relevant for the human health and simulating the transfer of contaminants in the unsaturated zone on different land use types - is described in the following.

KURZFASSUNG
Zur detaillierten Bewertung von Altlasten werden zunehmend Verfahren zur pfadübergreifenden Expositions- und Risikoabschätzung eingesetzt. Das methodische Konzept des UMS-Systems zur humantoxikologischen Bewertung der Schadstoffexposition des Menschen und des Schadstofftransfers in der ungesättigten Bodenzone bei verschiedenen Nutzungssituationen wird im folgenden dargelegt.

RÉSUMÉ
De plus en plus pour l´évaluation des sites contaminées avec une situation de danger bien différentiées on utilise avec succès également des méthodes de taxation de risques et d´éxpositions pour tous les chemins de polluants interdisciplinaire. Partant des principes homogènes pour l´évaluation des sites contaminées on propose pour le chemin d´effet sol-homme une minute pour l´évalution humano-toxicologique de l´éxposition de polluants à l'homme et pour le chemin d´effet sol-eau souterraine une méthode pour l´évaluation du transfères de polluants dans la zone non-saturée (le UMS-system).

Contaminated Soil '98, Thomas Telford, London, 1998, 301–309

1. Principles for the uniform assessment of abandoned contaminated sites

In its special reports on abandoned contaminated sites [1], the Council of Environmental Advisors called for the establishment of regulations uniformly applicable in the whole of Germany on risk assessment of suspected contaminated sites. This demand has been responded to by the submission of the Federal Soil Protection bill [2] and by joint activities of the Federal Government and the federal *Länder* (states).

The Federal Government/*Länder* working parties on soil (LABO), waste (LAGA) and water (LAWA) have reached agreement on uniform principles for the assessment of existing soil contamination and contaminated sites [3]. Based on these principles, a paper containing soil contamination levels triggering investigation („trigger levels") was presented by a LABO/LAGA working group for the soil - human pathway [4], and a LAWA/LABO/LAGA working group presented a paper on the soil - groundwater pathway [5]. The results of these Federal Government/*Länder* activities also serve as an important basis for the setting of trigger levels in legal regulations to be issued under the future Federal Soil Protection Act (BBodSchG). It is planned to establish use-specific trigger levels for direct soil - human contact [6] as well as trigger levels for the assessment of contaminant concentrations in leachate [7].

Future regulations concerning the management of suspected contaminated sites will thus derive from the provisions of the future BBodSchG, the more specific provisions of the legal regulations to be issued under this Act, as well as supplementary regulations of the various *Länder*. Supplementing the envisaged federal regulations relating to investigation and assessment, the *Länder* are free to establish requirements for the identification and historical exploration of suspected contaminated sites, for priority-setting with regard to assessment and remediation, for the assessment of groundwater contamination on the basis of water legislation provisions, for site-specific detailed investigations, as well as for the formulation of remediation objectives.

The future BBodSchG is to include the following requirements for contaminated sites assessment:

- a tiered procedure for the investigation and assessment of abandoned sites suspected of being contaminated and of other suspected contaminated sites;
- assessment of the results of the investigation on the basis of levels for contaminants in soil that either trigger further investigation (trigger levels) or the initiation of measures (action levels) and are specific to the various uses and protection-meriting assets;
- case-specific investigations when trigger levels are exceeded, in order to determine the nature and extent of the risk to affected targets as well as the exposure situation.

The use of a *tiered approach* ensures that the investigation is gradually extended in line with the information needs resulting from the respective stages. The object at the initial stage is to perform orientational investigations to determine, with the aid of trigger levels in particular, whether the suspicion of an existing risk is warranted or whether it essentially can be refuted. When trigger values are exceeded, more detailed investigations have to be performed in order to obtain a picture of the quantity, mobility and spatial distribution of the contaminants, of their dispersal in the various environmental media and of the extent to which they adversely affect targets.

While use- and target-specific trigger levels are to be regulated uniformly for the whole of Germany, such regulation is not envisaged for further-reaching schemes for *case-specific risk assessment*. Legally prescribing rigid procedures would not be appropriate, since such procedures are hardly able to take the differences in the special characteristics of the multitude of contaminated sites into account.

On the other hand, the extent to which individual soil values can depict the complexity and heterogeneity of the hazards that can emanate from contaminated sites is limited. Therefore, uniformly applicable principles consistent with the principles governing the derivation of trigger levels have to be formulated for subsequent case-specific assessment.

Against this background, the Federal Ministry for the Environment has funded a research project several years in duration, which was aimed at developing a concept for contaminated sites risk and exposure assessment covering several exposure pathways. Rather than representing a model in its own right, this concept sets out proposals for a toxicologically based evaluation of risks via the soil - human pathway as well as for the simulation of leachate transfer via the soil - groundwater pathway [8].

Decisions to be made in this context as to the necessity of remedial action are always determined by the existing relation between the site-related pollution load and the geogenic/anthropogenic background pollution in the individual case concerned. Imposing generally applicable requirements would not be appropriate at this stage. The UMS-system, an exposure and risk assessment model which takes the general assessment principles into account, is proposed in the following.

2. Concept for assessing risk and exposure for human health (UMS)

The UMS-system (U for environment, M for human health and S for pollutant substances) is a methodical aid for exposure and risk assessment of contaminated sites. UMS is to be used in particular for the case-specific detailed investigation of contaminated sites including former military and armament contaminated sites as well as in subsequent decision-making as to the need for remedial action. To evaluate the risks posed by contaminants to human health and to other targets UMS uses site-specific, *quantitative exposure assessment* methods. For this UMS defines 9 exposure scenarios:

• playground	• garden	• sports field
• fallow	• residential home	• industrial area
• public green	• commercial building	• well

In addition to pathway-specific assumptions, the description of the exposure situation is based on mostly empirically derived rates of uptake via different media such as soil, suspended solids and water as well as on anthropometric parameters such as body weight and age:

DIR = IR : BW x EFR (mg/kg BW x d)

DIR = daily intake rate
IR = user specific intake rate of contact media (e.g. soil, dust)
EFR = site and user specific exposure frequency
BW = user specific body weight

Against the background of the respective applications, parameters for use in exposure assessment have been proposed by a number of working groups. The Ad-hoc Working Group on Risk Analysis and Evaluation in Environmental Hygiene of the Environmental Hygiene Committee of the AGLMB has recommended „standards for exposure assessment" [9], drawing a general distinction between the „probable" and the „unfavourable" case. Assuming the worst case, the joint LABO/LAGA working group uses exposure factors for uptake via soil by ingestion and inhalation to derive soil levels [4, 10].

The UMS-system adopted the assumptions of the LABO/LAGA working group for cases involving „single-pathway analysis". For cases with complex exposure scenarios the concept recommends the use of a number of largely realistic assumptions formulated separately for uptake by ingestion, inhalation and the skin (see table 1). This responds to the demands made by AGLMB and ensures that in the assessment of multi-pathway exposure no cumulation of unfavourable assumptions occurs which might result in an overestimation of the risk emanating from the site concerned.

By means of the exposure factors and the measured concentrations of pollutant substances UMS calculates the *potential daily intake rate (***PDI**) of a pollutant:

PDI = CCM x DIR x R x AV (µg/kg x d)

PDI = potential daily intake rate
CCM = pollutant concentration
AV = biological availability for the exposure pathway soil oral
R = resorption factor

Table 1: Example for the derivation of daily intake rates

exposure scenario	exposure pathway	exposure groups	exposure frequency rate (EFR)	user specific intake rate of contact media (IR)	average daily intake rate (DIR)
Playground	soil/dust oral	K1	150 d_{et}/a relevant soil intake	250 mg soil/d	10,3 mg/(kg BW * d)
		K2	150 d_{et}/a relevant soil intake	150 mg soil/d	3,1 mg/(kg BW * d)
		L		weighted sum of DIR/70 a	1,03 mg/(kg BW * d)
	soil dermal	K1	150 d_{et}/a relevant soil contact	3000 cm^2 exposed skin surface (= 50 % of 0,6 m^2)	1250 cm^2
		K2	150 d_{et}/a relevant soil contact	4000 cm^2 exposed skin surface (= 40 % of 1,0 m^2)	1650 cm^2
		L		weighted sum of DIR/70 a	310 cm^2
	dust inhalative	K1	75 d_{et}/a and 2 h/d relevant activity with dust emission	inhalation rate 0,5 m^3/h, 1 mg dust/m^3 air, 0,66 moisture factor, 75% retention, 40% inhalative intake (⇒ 0,1 mg dust/h)	0,0041 mg/(kg BW * d)
		K2	75 d_{et}/a and 2 h/d relevant activity with dust emission	inhalation rate 0,7 m^3/h, 1 mg dust/m^3 air, 0,66 moisture factor, 75% retention, 40% inhalative intake (⇒ 0,14 mg dust/h)	0,0029 mg/(kg BW * d)
		L		weighted sum of DIR/70 a	0,00065 mg/(kg BW * d)
Industrial area	dust inhalative	E_1	220 d_{et}/a, 8h/d (5 h/d average working hours)	inhalation rate 1,7 m^3/h, 0,325 mg dust/m^3 air, 75% retention, 0,66 moisture factor, 40% inhalative (⇒ 0,55 mg dust/d)	0,0078 mg/(kg BW * d)
		L_1		weighted sum of DIR/70 a	0,0033 mg/(kg BW * d)
		E_2	110 d_{et}/a, 8 h/d (2,5 h/d working hours with dust emission)	inhalation rate 1,7 m^3/h, 5 mg dust/m^3 air, 75% retention, 0,66 moisture factor, 40% inhalative (⇒ 4,20 mg dust/d)	0,060 mg/(kg BW * d)
		L_2		weighted sum of DIR/70 a	0,026 mg/(kg BW * d)
	soil/dust oral	E	100 d_{et}/a relevant soil intake	30 mg/d (⇒ 8,22 mg soil/d)	0,12 mg/(kg BW * d)
		L		weighted sum of DIR/70 a	0,05 mg/(kg BW * d)

(K1 = infants, K2 = children, E = adults, L = lifetime)

The PDI represents the dose of a pollutant resorbed by the human body. One or more pathways of exposure such as oral intake of soil, oral intake of potable water, inhalation of dust etc. may be attached to any exposure scenario. The calculated dose rates for the oral and the inhalative intake pathway are summed up:

$$PDI_{oral} = PDI_{oral\ soil/dust} + PDI_{oral\ water}$$

The use of harmonised assessment principles ensures mutual consistency between the principles underlying the derivation of soil levels for the soil - human pathway and those of the concept developed for case-specific risk evaluation.

To satisfy the legal requirements regarding the averting of danger, it was necessary to derive a *hazardous body dose*, i.e. that dose of a contaminant at which an adverse effect on human health is first observed. Derived specific to the different routes of uptake, these hazardous body doses [4, 11] serve as the toxicological basis for risk evaluation and for the derivation of trigger levels uniformly applicable in the whole of Germany.

The toxicological data base is composed of human-toxicity data in the form of tolerable resorbed dose rates (TRD values), which were compiled on behalf of the Federal Environment Ministry and the LAGA for 82 substances/groups of substances of relevance for contaminated sites [9]. TRD-values are total body doses of a hazardous substance for which no adverse effects on health are to be expected [7]. For cancer effects the risk index is calculated in terms of lifetime probabilities by the PDI value over the unit risk (10^{-5} equivalent dose rate). For toxicological assessment specific *risk indices* (RI) for each intake pathway are calculated by division of the evaluated PDI with the tolerable dose rates (TRD):

$$RI = PDI / TRD$$

The risk index (RI) describes the extent to which the tolerance threshold is undershot or exceeded. If this risk index is lower than 1, no risks exist and if the risk index exceeds 1 impacts on human health cannot be excluded, based on our substance-specific knowledge of dose-effect relationship [5].

The risk indices of all intake pathways involved in one exposure scenario are summed up and transformed to risk values (RV) by an assessment function.

In addition, there is the need to get a better picture of the uncertainty and variation ranges of exposure assumptions by exploring these questions on the basis of a variety of practice-oriented cases, with the objective of improving scientific knowledge about further exposure pathways such as dust inhalation and dermal contact with selected relevant substance. In an overall

assessment, *local background concentrations* and other substance-specific knowledge about ubiquitous background pollution must be taken into account in the interpretation of the results obtained, in order to determine the extent to which the contaminated site contributes to the pollution load and thus substantiate the necessity and urgency of contaminated site remediation.

Further research needs in this field include in particular research aimed at improving scientific knowledge about matrix-specific bioavailability, resorption in the body, the toxicological data base for substances and substance mixtures frequently present at contaminated sites such as PAHs, BTEX, volatile halogenated hydrocarbons, and nitroaromatics, the evaluation of possible synergistic effects, and the management of carcinogens.

The procedure of the UMS-system reflects the recommendations of the US EPA, according to which rather conservative exposure assumptions are replaced by more realistic, site-adapted ones as the investigation of the site progresses and knowledge about it increases [12, 13].

In cases in which a sound empirical data base is available, it is advisable to use probabilistic methods in place of these deterministic exposure assumptions. Probabilistic methods are currently being discussed intensively in the Netherlands and in the US EPA, so that it can be expected that further experience and knowledge will be acquired in this field.

3. The UMS-module SISIM to simulate the transfer of contaminants in the unsaturated zone

For statements about the quantity and moment of groundwater contamination suggestions are necessary, which describe the transport of contaminants in the unsaturated zone. For this the pollutants transfer model „SISIM" was developed, which is an additional module of the UMS-system. A peculiarity of SISIM is that you can show the movement of the contaminated water as well as the distribution of concentration in soil changing with time and location on the screen.

Input parameter are the characterization of the different soil layers (content of clay, organic matter, volumetric water content, residual volumetric water content, bulk density, total porosity and the saturated hydraulic conductivity), the sampling point and depth, the analyzed concentrations of the different contaminants as well as the average infiltration of rainwater).

SISIM is based on equilibrium states that are calculated by partition coefficient considering the physical and chemical characteristics of pollutants. It is supposed that an equilibrium state in the soil system is reached immediately, so that the concentrations in the three soil phases „matrix, water and air" can be calculated easily.

The calculation of the vertical pollutant transport in the unsaturated zone is based on a cascade model. The transport model computes the distribution of contaminants for every soil in time and location. The calculations are carried out until the capillary zone of the groundwater is reached. The last soil layer marks the point evaluating the extent of the damage referring to the groundwater.

The results of SISIM are the concentrations of contaminants in soil and percolating soil water for every soil layer in time and location. Based on these information the extent of groundwater damage is calculable and soil screening levels derivable.

4. Acknowledgement

The authors would like to thank Mrs. Coan, Federal Environmental Agency, Berlin, for the good job she did translating the main parts of this paper.

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DETERMINATION OF RISK-BASED EXPLOSIVES CONTAMINATION GUIDELINE VALUES IN SOILS USING THE CLEA MODEL

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Key words: Explosives, exposure model, guidelines, risk analysis, trigger values, military sites, warfare-related contaminated sites, planning, remediation.

Contaminated Soil '98, Thomas Telford, London, 1998, 311–319

INTRODUCTION

Areas of land associated with the explosives industry, munitions manufacture and defence-related activities can present special hazards or difficulties during their investigation, risk assessment and remediation. Acute hazards such as explosion of energetic material or munitions are immediately evident, albeit their identification and associated risk assessment require specialist skills.

Energetic compounds present certain human health and environmental hazards in addition to those of explosion. The need to assess risks posed by land contaminated by explosives and to identify appropriate remediation targets, is no less important for those compounds than for other substances encountered in conventional site assessments. The extensive present and historical land holdings of defence-related industries highlights the need for appropriate soil guideline values.

This paper outlines the context, objectives and methodologies being used in the UK to establish risk-based guideline values for explosives contamination. The special challenges posed are discussed, and research requirements are identified.

The project is a joint undertaking of British Aerospace Royal Ordnance, CRBE, the Department of the Environment, Transport and the Regions (DETR), the Environment Agency, ICI Explosives and the Ministry of Defence (Defence Evaluation and Research Agency - DERA).

THE CIVIL AND DEFENCE EXPLOSIVES INDUSTRIES - HISTORICAL CONTEXT AND LANDHOLDINGS

Use of land for munitions manufacture in the UK dates back many centuries. The first British production of gunpowder is described in the 13th century records of Roger Bacon (ICAC 1909). Well known sites such as the Royal Woolwich Arsenal and the Royal Gunpowder Factory at Waltham Abbey have only recently been decommissioned - to present the temporal context, Guy Fawkes allegedly obtained his famous gunpowder from the latter site in 1605.

Areas of land involved with the defence industry are considerable. For example, Royal Ordnance (RO), the UK's largest munitions manufacturer, has a contemporary landholding of about 3,000 hectares comprising 14 munitions manufacturing sites - in 1945 there were about 60 RO sites in operation across England, Scotland and Wales.

In addition to these sites are those for civil explosives manufacture, MoD storage and training facilities, and research facilities. The greatest use of land for civil explosive manufacture coincided with the Industrial Revolution in the 18th and 19th centuries. Following the breakthrough to modern detonating explosives with the discovery of nitroglycerine in 1846 and its stabilisation into 'Kieselguhr ' by Nobel in 1866 to form dynamite, the modern explosives industry was born. In 1871, Nobel set up his first factory in Britain in Ardeer in the West of Scotland, and by 1940, there were more than 100 commercial explosives manufacturing sites in the UK.

SURPLUS LAND

The civil explosives industry has declined substantially over the last 50 years, following the demise of the British deep mined coal industry, growing international trade in high explosives and competition from new explosive products. In parallel to this, defence-related explosives manufacture has itself declined over the same period. This has been especially marked over the last decade following the end of the cold war. Coupled with different working practices and political climates, the decline in munitions demand has left the UK and overseas defence industries with massive over-capacities. Far more land is owned for defence related use than is currently required. Furthermore, much of this land is derelict, presenting a wasted resource for the UK and for local communities around such sites, themselves impacted by the loss of local employment from the sites.

To bring former defence and explosives industry land into alternative use requires the spectrum of planning, risk assessment and remediation activities well known throughout the redevelopment industries. However, the special nature of these sites presents a number of untypical challenges unique to the industries involved. These form the subject of a separate paper in these proceedings (Birnstingl and Smith 1998).

The key to risk assessment and site redevelopment is the establishment of appropriate contamination thresholds for hazardous compounds that may be present. Many of the industrial activities utilised in the explosives manufacturing and defence industries are common to other industrial activities. For example, many sites have underground fuel storage tanks, fuel filling facilities and even acid manufacturing plants. For many of the contaminants that may potentially arise from these processes, contamination guideline values have been/are being developed (ICRCL 1983, 1987; Ferguson & Denner 1994, 1998). However, guideline values for explosive compounds have not been developed to date.

THE ROLE OF GUIDELINE VALUES IN RISK ASSESSMENT

The idea of using generic guideline values as a tool to promote consistent and cost-effective assessment of contaminants in soil dates back to the late 1970s in the UK (ICRCL 1979) and the early 1980s in the Netherlands (VROM 1983). The idea was resisted in the USA at the Federal level until the 1990s although several States had independently developed their own guideline values (e.g. Massachusetts, California, Michigan).

Some of the early guideline values did not have an explicit risk-based derivation. Many users of the guidelines did not understand the basis for their derivation and therefore could not judge when to use them appropriately and when not to. In the UK the trigger values published by the Interdepartmental Committee for the Redevelopment of Contaminated Land (ICRCL 1983, 1987) covered only a limited range of contaminants, and action trigger levels were published in 1987 only for contaminants associated with gasworks and other coal carbonisation processes.

In recent years there has been an increasing tendency to derive guideline values using risk-based models in which the exposure and other assumptions are made explicit.

Examples of model used by national governments for developing risk-based guidelines are CSOIL in the Netherlands (van den Berg *et al* 1993), UMS in Germany (Hempfling *et al* 1997) and CLEA in the UK (Ferguson & Denner 1994, 1998). The Soil Screening Levels published by the USEPA in 1996 are also based on a consistent and explicit set of exposure assumptions (USEPA 1996). These risk-based approaches make it much easier for the various stakeholders to recognise the strengths and limitations of the guidelines, and to derive alternative guidelines when the generic exposure assumptions do not apply for any particular site.

THE UK CONTEXT

The development of UK Government policy on contaminated land has been guided by a number of central objectives (UK Department of the Environment/Welsh Office 1994) including prevention of pollution, sustainable development, and a 'suitable for use' approach to land remediation.

Section 57 of the Environment Act 1995 inserts a new Part IIA into the Environmental Protection Act 1990 and in the future this will be the basis of the regulation of land which in its current use is contaminated. Statutory guidance will provide much of the detail of the operation of the new regime and, within the context of the primary legislation, provide the flexibility needed to deal with the situations met with on specific sites. The DETR issued draft statutory guidance for consultation in September 1996: it will be revised before Part IIA comes into operation.

Contaminated land is defined in the Environment Act 1995 as "... any land which appears to the local authority in whose area it is situated to be in such a condition, by reason of substances in, on, or under the land, that

(a) significant harm is being caused or there is a significant possibility of such harm being caused; or

(b) pollution of controlled waters is being, or is likely to be, caused."

In determining whether significant harm is being caused or there is a significant possibility of such harm being caused, either site-specific risk assessment or use of guideline values will be permitted. Of course, any risk assessment based on guideline values must demonstrate that the values are appropriate and relevant for the use and characteristics of the land in question. The draft statutory guidance (UK Department of the Environment 1996) is explicit on this:

"In using any guideline values, the local authority should be satisfied that:

(a) the guideline values are relevant to the judgement of whether the effects of the pollutant linkage in question constitute a significant possibility of significant harm;

(b) the assumptions underlying the derivation of any numerical values in the guideline values (for example, assumptions as to the soil conditions, the

behaviour of potential pollutants, the existence of pathways, the land-use patterns, and the availability of receptors) are relevant to the circumstances of the pollutant linkage in question;

(c) any other conditions relevant to the use of the guideline values have been observed (for example, the number of samples taken or the methods of preparation and analysis of those samples); and

(d) appropriate adjustments have been made to allow for the differences between the circumstances of the land in question and any assumptions or other factors relating to the guideline values.

The local authority should be prepared to reconsider any determination based on such use of guideline values if it is demonstrated to the authority's satisfaction that under some other more appropriate method of assessing the risks the determination would not have been made."

The guideline values being developed for DETR and the Environment Agency using the CLEA model are based on generic assessment of ***direct risks to human health*** from exposure to contaminated soil. They cover a variety of substances potentially arising from contaminative site uses, but not explosive substances. Hence the decision to set up the project reported here.

It is more difficult to develop generic soil guidelines for groundwater protection. This is because most of the key variables (thickness and attenuating capacity of soil and bedrock, depth to water table, source protection zone status, etc.) are highly site-specific. The Environment Agency has developed a risk-based approach for assessing the significance of soil contamination in the context of groundwater pollution (Environment Agency 1996a, b).

Similarly, transfer of contaminants from soil to surface waters is highly site-specific and depends on run-off volume, peak flow rate, soil erodability, slope length and steepness, sorption capacity of the soil, vegetation cover type, and distance to receiving body. For many sites the major threat to surface water quality is likely to occur during site redevelopment, and will need to be assessed on a site-specific basis.

The definition of contaminated land in Part IIA not only includes its effect on the health of man but also its effect on other living organisms of ecosystems and on property. The draft statutory guidance advises that authorities will need to consider, for example, irreversible change in the functioning of a habitat protected by the Wildlife and Countryside Act 1981, and structural failure or substantial damage to buildings.

THE CLEA MODEL

The Contaminated Land Exposure Assessment (CLEA) model was developed by CRBE under contract to the Department of the Environment. Although it can be used for site-specific risk assessment, it was developed specifically for deriving human health Guideline Values to help determine whether "significant harm is being caused or there

is a significant possibility of such harm being caused" from exposure to contaminated soil. Ten exposure pathways are included as summarised below.

- Outdoor ingestion of soil
- Indoor ingestion of dust
- Consumption of home-grown vegetables
- Ingestion of soil attached to vegetables
- Skin contact with indoor dust
- Outdoor inhalation of fugitive dust
- Indoor inhalation of dust
- Outdoor inhalation of soil vapour
- Indoor inhalation of soil vapour

If no information on background exposures is available, CLEA can compute a very rough estimate based on the contaminant concentration in mains water supply. Intake is then estimated via three separate routes: ingestion of drinking water from mains supply; skin contact with mains water during showering and bathing etc; inhalation of vapour during showering and bathing, and from ambient concentrations otherwise derived from mains water (e.g. cooking, washing machines, dishwashers). It is recognised that such estimates may be poor indicators of background exposure, especially for lipophilic or highly volatile substances.

No general assumption can be made about contaminant concentration in mains water. But for the purpose of roughly estimating background exposure, a possible approach is to use the maximum permitted level for the relevant contaminant in drinking water. Over-estimation of intake from the three water-related pathways would thus compensate, at least in part, for neglect of intakes via other pathways (food etc.). For some substances background exposure is considered to be negligible.

The relative importance of the different pathways will depend on the contaminants, and on site use which is assumed to fall into one of the following categories: residential with gardens; residential without gardens; allotments; parks, playing fields and open space; commercial/industrial.

In CLEA, contaminant intakes are calculated incrementally for 18 age intervals. The first 16 intervals correspond to the first 16 years of life, the 17th interval is the working life (taken as 16 - 59), and the 18th is 60 - 70 years. The user then has the choice of calculating an average daily intake with any averaging period up to a maximum of 70 years.

Time dependent effects

Because natural removal processes will gradually reduce the concentration of many contaminants in surface and near-surface soils, all exposure equations are written with concentration as a time-varying parameter. Removal processes include photolysis, chemical reaction, volatilisation, biodegradation, run-off, erosion, leaching and crop offtake. Biodegradation is particularly important in determining risks from organic contaminants, but the rate of degradation is highly site-specific and depends on the

types and growth rates of microbial populations which in turn are influenced by moisture content, temperature, pH, Eh, nutrient availability and toxicity.

Most risk assessment models provide no explicit means for modelling natural attenuation of contaminants. In contrast environmental models developed specifically for organics (e.g. Jury *et al* 1983) usually represent chemical and biological degradation of organic contaminants as a single first order process with rate constant specified by the user. This is the approach adopted for the CLEA model. Thus if the initial concentration is *Co* and first order decay is assumed, then the concentration at time *t* is

$$C_t = Co\ exp\ (-kt)$$

and the average concentration C_i over the time interval $(\Delta T)_i = t_i - t_{i-1}$ is given by

$$\overline{C_1} = \frac{C_0}{(\Delta T)_i} \int_{t_{i-1}}^{t_i} \exp(-kt)dt$$

Incorporating a first order decay term can have a dramatic impact on soil Guideline Values. Published half-lives (half-life $t_{1/2}$ = ln (2)/k) are often based on laboratory experiments using pure compounds. These degradation rates may be very much faster than those applying to contaminants in complex mixtures degrading under field conditions. It also needs to be recognised that many organic contaminants may not degrade completely and that a residual level may persist (Beck et al 1995) representing an intrinsic kinetic constraint on biodegradation. It seems likely that this kinetic constraint is related to ageing, which is well recognised in organic contaminants and probably involves a combination of diffusion into micropores, partitioning into soil organic matter, and strong surface adsorption (Hatzinger & Alexander 1995). This means that, on old industrial sites, many of the organic contaminants that are going to degrade naturally (i.e. without engineering intervention) will already have done so. Therefore great caution needs to be exercised in choosing a contaminant half-life in soil.

Variability and uncertainty in model inputs are handled probabilistically in CLEA using the Monte Carlo method. The essence of Monte Carlo exposure modelling is that single-point values of certain key variables are replaced by probability density functions (PDFs) reflecting the variability or uncertainties associated with exposure parameters. Each pass through a Monte Carlo model involves random sampling from the relevant PDFs to produce a single estimate of intake. Multiple passes thus allow a distribution of intake to be built up. Often the most difficult aspect of Monte Carlo modelling is choosing appropriate PDFs for the key variables. In the CLEA model, users can choose from the following PDFs: uniform, normal, lognormal, triangular, beta and gamma.

DATA REQUIREMENTS AND RESEARCH NEEDS

The current study focuses on the following explosive substances:
Nitrocellulose (NC), Nitroglycerine (NG), Nitroguanidine (Picrite), Trinitroluene (TNT), Cyclotrimethylenetrinitramine (RDX), Cyclotetramethylenetetranitramine

(HMX), Pentaerythroltrinitrate (PETN), Ethyleneglycol dinitrate (EGDN), Trinitro 2, 4, 6 - phenylmethylnitramine (Tetryl), Hexanitrostilbene (HNS), Picric Acid, 2, 4 - and 2, 6 - Dinitrotoluene (DNTs), Amino DNTs (degradation products of TNT).

There is a vast body of research on the explosive characteristics of these materials, and a considerable amount of information on acute toxicity. However there is a relative dearth of information on chronic toxicity, and very little information on fate and transport in soil and groundwater at levels of potential environmental concern. Information gaps and research needs are highlighted below:

- plant uptake
- dermal uptake
- tolerable daily intake
- compound fate and transport in soil and groundwater
- chronic and acute health effects of compounds present in mixtures
- influences of other contaminants

CONCLUSIONS

When completed this project will have derived soil guideline values for a variety of explosive substances, which will help to promote consistent and cost-effective assessment of sites potentially contaminated by explosive substances. This project has been made possible by joint funding from Government and public bodies (DETR, the Environment Agency, and the Ministry of Defence) and industry (British Aerospace Royal Ordnance and ICI Explosives), and co-operative research with an academic partner (CRBE).

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HUMAN EXPOSURE MONITORING AND BIOAVAILABILITY ISSUES

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Key words: Arsenic, bioavailability, contaminated soil, exposure, human health risk, lead, monitoring, soil, risk assessment, toxicity

SUMMARY
Human exposure monitoring through the analysis of contaminant concentrations in suitable biological media provides valuable information for the risk assessment of contaminated sites. The association between soil lead levels and blood lead levels in children living in urban, smelter and mining communities is one example. The association (slope factor) largely depends on the bioavailability of the contaminant in a soil matrix. Experimental animal systems to test the bioavailability of soil contaminants are being developed, and the uptake and toxicity of arsenic in soil from three wood treatment plants is presented as an example.

KURZFASSUNG
Die Gesundheitsüberwachung der Bevölkerung durch Messung der Konzentrationen von Gefahrstoffen in geeigneten biologischen Substraten liefert wertvolle Informationen zur Risikoabschätzung kontaminierter Gegenden. Der Zusammenhang zwischen der Bleibelastung in der Umwelt und dem Gehalt an Blei im Blut von Kindern, die in Grossstädten und in Gegenden wohnen, in welchen Schmelz- und Bergwerksarbeiten durchgefuehrt werden, ist ein Beispiel. Dieser Zusammenhang zwischen Umweltgehalt und Blutgehalt des Gefahrstoffes, dargestellt durch den Steigungsfaktor, hängt grösstenteils von dessen Bioverfügbarkeit im Boden ab. Tierexperimentelle Ansätze zur Erforschng der Bioverfügbarkeit und Toxizität von Gefahrstoffen im Boden werden derzeit entwickelt. Die Aufnahme und Giftigkeit von Arsen aus Bodenproben von drei verschiedenen Holzimprägnierungsanlagen wird als Beispiel vorgestellt.

RÉSUMÉ
Une contribution importante à l'évaluation des risques posés par les sites contaminés est fournie par l'analyse d'indicateurs biologiques appropriés. Il y a, par example, covariation entre les taux de plomb dans les sols et dans le sang, chez les enfants habitants à proximité d'industries ou de mines, ou dans de larges agglomérations. La pente décrivant l'association dépend en grande partie du taux d'absorption biologique. Des systèmes expérimentaux ont été mis en place afin d'étudier chez l'animal l'absorption et la toxicité des pollutants des sols, et sont illustré ici en relation à l'arsenic contenu dans le sol de trois différentes usines d'imprégnation du bois.

Contaminated Soil '98, Thomas Telford, London, 1998, 321–329

Introduction

Toxic chemicals in soil may endanger the environment as well as the health and general well-being of people living at our near the contaminated site. These sites represent an ongoing threat and inproperly remediated sites may result in long-term exposure to residual contaminants among the residents as well as accidental exposure, for instance during maintenance work. Several possible pathways of direct and indirect human exposure to soil contaminants are summarized in Figure 1.

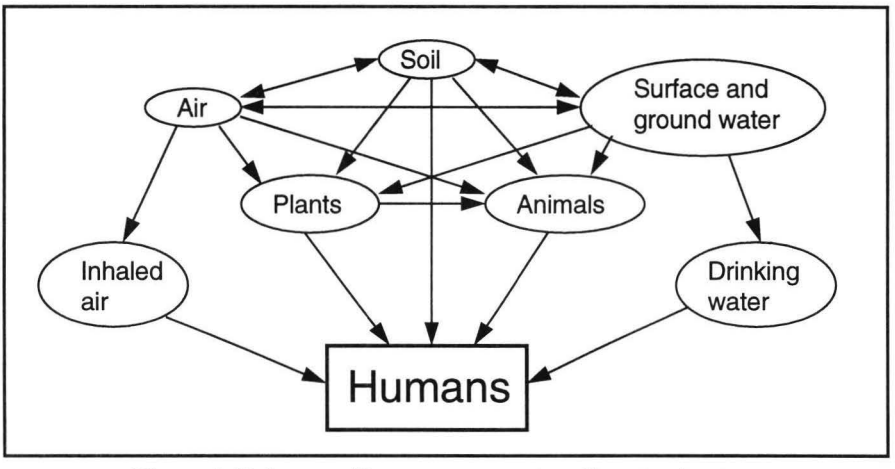

Figure 1. Pathways of human exposure to soil contaminants.

Small children are generally considered to be the primary risk group for direct exposure to soil contaminants due to their mouthing behavior. Ingestion of contaminated soil and dust may occur when dirty fingers or hands are put in the mouth or via dirty objects such as toys, candy etc. Exposure to soil contaminants may also occur though the inhalation of vapors and respirable soil dust particles. Volatile substances may penetrate building materials and contaminate indoor air, especially in confined spaces underground. This problem has mainly been considered in the case of residential radon exposure. Some chemicals may cause systemic effects as the result of dermal uptake or directly affect exposed skin areas and cause ulceration, inflammation and allergic dermatitis. The absorption of compounds upon dermal exposure is largely determined by their lipid solubility. Soil contaminants may migrate to ground and surface water or penetrate plastic water pipes. Use of contaminated water as drinking water or for food preparation may result in contaminant exposure through ingestion. Plants and vegetables grown at or near a contaminated site may be contaminated through the deposition of soil dust particles on leafy surfaces or via root uptake of contaminants from soil pore water. Human exposure to environmental contaminants via plants and vegetables has mainly been considered in industrial areas, but the agricultural use of pesticides and sewage sludge has also raised concern. Environmental contaminants may accumulate in lake sediments and bioaccumulate in aquatic organisms and fish inhabiting affected waters. This is for instance seen in areas contaminated by mercury and persistent organic compounds, such as PCBs. Persistent lipid soluble contaminants may also accumulate in meat and milk of grazing cattle and be a potential source of human exposure. Cattle are exposed both via the plants themselves and through the ingestion of soil while grazing.

Human exposure monitoring

A quantitative estimation of exposure to soil contaminants is an important part of the risk assessment process. The risk depends not only on the inherent toxicity of the chemicals in question but also on the route, frequency and duration of exposure. Toxicity data, including dose-response relationships, are usually derived from animal experiments using pure chemicals under well-defined laboratory conditions, a situation far from that encountered in an environmental setting. Exposure assessment can be based on environmental monitoring, such as air, water, food and soil sampling and analysis. From these data, human exposure can be estimated through modelling by use of pathway-specific exposure factors, such as breathing rate, food and soil ingestion rates etc (McKone & Daniels, 1991; Calabrese & Stanek, 1995). Several investigators have tried to develop methods to estimate soil ingestion rates for children. One method is based on the use of certain elements frequently found in high concentrations in soil, but not in food or drinking water, and poorly absorbed in the gastrointestinal tract. The amount of soil ingested can be calculated from the concentration of the element in soil and feces. Recent estimates (Calabrese & Stanek, 1995) suggest that the average small child may ingest about 0.1-0.2 g soil daily, while children with pica-behaviour (a craving for inedible items as food) may ingest substantially larger amounts (3-10 g). However, in order to obtain more reliable data on actual human exposure to chemicals, techniques for individual exposure monitoring have to be utilized. Human tissue and fluid specimens have been used to monitor exposure to environmental contaminants such as heavy metals and persistent organic compounds. The analyses may include the parent compound, its metabolites and excretion products or complexes formed between reactive products derived from the compound and macromolecules such as proteins and DNA. Basic knowledge on contaminant uptake, distribution, metabolism and excretion as well as mechanisms of target organ toxicity is essential in order to correctly interpret the data obtained (Fig. 2).

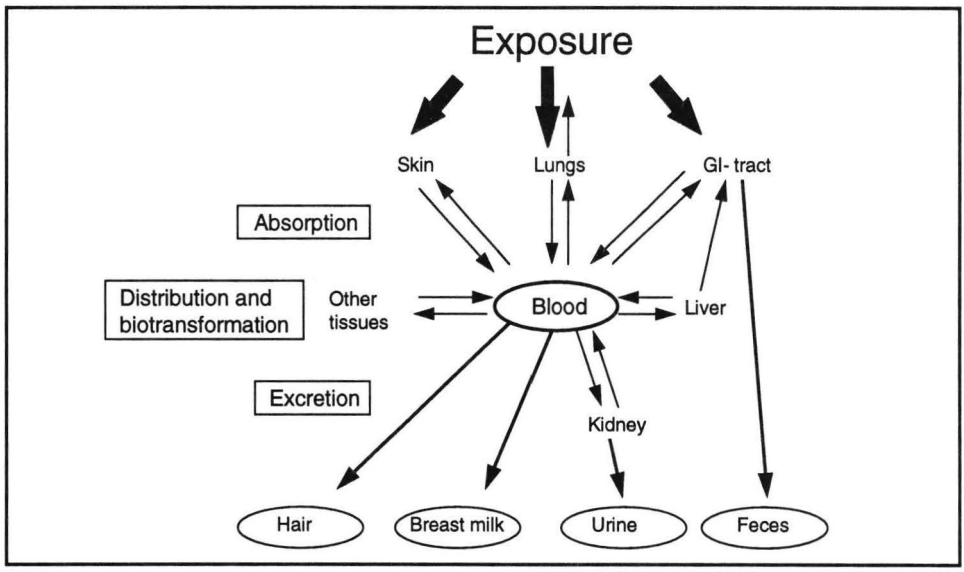

Figure 2. Pathways of absorption, distribution and excretion of chemicals. Specimens commonly used for human biomonitoring of exposure are indicated.

Human biomonitoring of exposure to soil contaminants has primarily focused on lead, which is an important environmental problem due to its use as a gasoline additive and in paint. Although it is evident that the introduction of unleaded gasoline in several countries has led to a decline in the blood lead levels it is estimated that several million children in the US alone still show blood lead levels above 100 µg/l, the level of concern defined by the CDC. The health effects associated with lead exposure have raised concern in mining and smelter communities where the lead levels in soil may be high. Urban areas also show substantially elevated soil lead levels which may be associated with high exposure, especially among small children. A recent study in urban and suburban Stockholm showed that the median lead level in Stockholm city park soil was 100 µg/g, substantially higher than in the neighboring suburban communities (Berglund et al., 1994). However, the concentration of lead in blood of young children (1-4 years of age) was similar. A study on the blood lead levels in children in two mining communities in central Sweden showed slightly higher concentrations than in the Stockholm study (Bjerre et al., 1993), but still below 100 µg/l. However, the blood lead levels increased during the summer season, indicating an increased exposure during the summer months, probably related to outdoor activities and more frequent contact with soil and dust. This is illustrated in Figure 3. It should be noted that the bar showing blood lead levels in children from Stockholm city represents a subset of the children (highest quartile of blood lead levels). Seasonal differences in blood lead levels have also been observed by other investigators (Johnson et al., 1996). Exposure to soil contaminants does not necessitate outdoor activities, as outdoor soil contribute considerably to indoor house dust. Thus, levels of toxic chemicals in indoor dust will be elevated in contaminated areas, and may even exceed the outdoor soil levels.

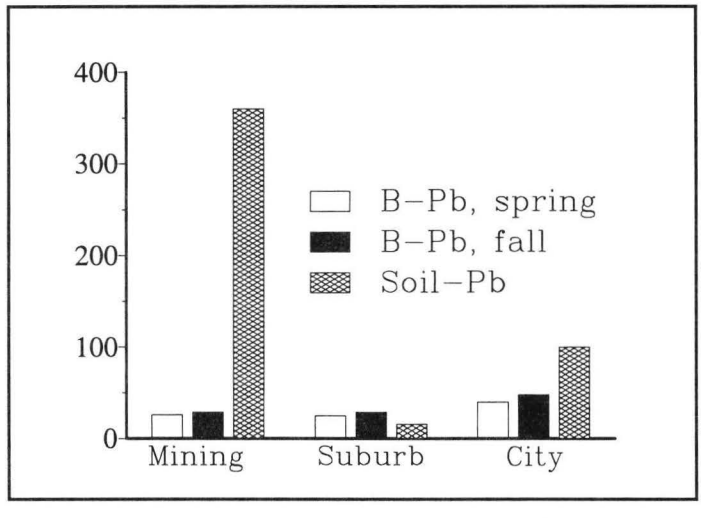

Figure 3. Seasonal variation in blood lead levels (µg/l) in small children (1-4 yars of age) in relation to soil lead levels (µg/g) (data from Bjerre et al., 1993; Berglund et al., 1994).

Bioavailability

The term bioavailability is used in order to define the fraction of a chemical that is absorbed by an organism following exposure through ingestion, inhalation or dermal contact. The bioavailability of the contaminant is the primary factor that will determine the ultimate target dose and consequently the risk for adverse effects in the target organ. The bioavailability of chemicals in a soil matrix is determined by soil-specific factors, such as the particle size distribution and organic matter content, along with various physiological factors (age, nutritional staus etc) characterizing the exposed organism. The default assumption in environmental monitoring and exposure modelling is usually that the fractional uptake of a specific chemical in a soil matrix is similar to uptake via food (Bowers et al., 1994).

A number of studies have found elevated lead levels in the blood of children living in areas where the soil lead levels are high, such as mining and smelter communities as well as inner-city residential areas. However, the relationship (slope factor) between soil lead concentration and blood lead level is not simply described (Steele et al, 1990; Madhavan et al., 1989). The slope factor for lead in blood versus lead in soil depends on the source of contamination. The slope factor in urban communities and communities with operating smelters have been shown to have a higher value than the slope factor found in studies on blood lead levels in residents of mining communities, suggesting a lower bioavailability of lead in soil in the latter (Steele et al., 1990).

The bioavailability issue can be addressed by combining chemical analysis of soil samples with tissue analysis of wild species of animals living in a contaminated habitat (Pascoe et al., 1994; Ma et al., 1991; Stansley & Roscoe, 1996). An alternative approach is to or household pets in communities affected by environmental contamination (Berny et al., 1994). In recent years, the bioavailability of soil contaminants have also been studied in experimental animals under well-defined laboratory conditions. The bioavailability of chemicals in a soil matrix can be tested by adding known concentrations of pure chemicals to uncontaminated soil samples or by testing the uptake of chemicals from soil samples obtained from contaminated areas. The first approach allows the use of radiolabeled test chemicals whose distribution and metabolism can be easily monitored in animal experiments, and results have shown that the absorption of pure chemicals in the gastrointestinal tract may be reduced if delivered in a soil matrix (Freeman et al., 1996; Schilderman et al., 1997). The second approach is more relevant for risk assessment as it address the question of interaction among different forms of one or several chemicals in a contaminated soil sample. The experiments typically involves young animals, primarily rats, that are administered samples of contaminated soil in a food mixture. The uptake of a specific contaminant can be monitored by blood and tissue analyses (Vahter, 1988; Freeman et al., 1992; 1993; 1994; 1995; Schoof et al., 1995; Buchet et al., 1995; Groen et al., 1994; Dieter et al., 1993). One recent example is the use of a juvenile swine experimental model in order to assess the bioavailability of lead in soil from the Smuggler Mountain Superfund Site (Casteel et al., 1997). The bioavailibility of soil lead relative to orally administered soluble lead (lead acetate) was found to range from 56 to 86%, corresponding to an absolute bioavailability of 28-43%.

Copper, chromium and arsenic salts are used for the preservation of wood and wooden structures. The soil at former wood treatment facilities may thus be highly contaminated by arsenic (>1000μg As/g soil). In a study performed at our institute (Vahter, 1988), the toxicity of arsenic in soil samples obtained from three former wood treatment plants was tested in mice. The animals received arsenic in the form of a food-soil mixture and signs of toxicity

within 72 hours was recorded. The concentration of arsenic in the three soils referred to as 1, 2 and 3 in the tables below was 9000, 1100 and 1400 µg/g, respectively. The mice were starved for 36 hours preceeding the experiment. Soil samples were mixed with ground food pellets and sugar. By adding water, a thick paste of the mixture was obtained. The food mixture contained 10-75% soil, 10-40% pellets and 10-23% sugar. The highest dose of As administered corresponded to 400, 51 and 60 mg As/kg for soil 1, 2 and 3, respectively. The toxicity of the soil samples showed a pronounced variation that was not related to their arsenic content (Table 1.).

Table 1. Toxicity of arsenic in soil from three wood treatment plants. Data from Vahter (1988).

No. of mice	Food mix	Ingested	mg As/kg bw	Toxicity
5	10% soil 1	80%	50	None
5	40% soil 1	50%	270	None
5	58% soil 1	80%	400	None
2	28% soil 1	75%	125	None
2	39% soil 1	75%	250	None
5	75% soil 2	80%	51	All affected, one died
5	33% soil 2	80%	39	All affected, one died
2	40% soil 3	75%	35	None
2	55% soil 3	75%	52	None
3	75% soil 3	75%	60	All affected, one died
5	33% soil 3	75%	48	All affected, no deaths

The LD_{50} for arsenic administered as sodium arsenate in drinking water was found to be 35-40 mg/kg body weight. A tenfold higher dose of arsenic in the form of soil 1 had no effect on the animals. A substantially lower dose of arsenic administered via soil sample 2 showed a high degree of toxicity and 2 out of 10 animals in the test group died. With test soil 3, one out of 12 animals died at a dose level of 50-60 mg As/kg.

The concentration of arsenic in blood, liver and kidneys two or four hours after ingestion of arsenic-containing soil or administration of radiolabeled (^{74}As) sodium arsenate was measured. The higher toxicity of arsenic in soil 2 and 3, as compared to soil 1, was related to a higher bioavailabilty of arsenic as reflected by the tissue concentrations in relation to administered dose (Table 2). 110 mg As in soil 2 resulted in the same tissue concentration of arsenic as four times higher dose of arsenic in the form of soil 1. The highest tissue levels of arsenic were seen in animals given 120 mg As in the form of soil 3. The basis for this difference is not known. It may be due to differences in the type of arsenic compounds initially used at the plants, different forms of arsenic in the soil, particle size, soil pH, adsorption of arsenic to organic material in the soil etc.

Table 2. Concentration of arsenic in the liver and kidneys of mice two (N=3) and four (N=2) hours following ingestion of arsenic-containing soil. Data from Vahter (1988).

Soil mix	Dose mg As/kg	2 hours, mg As/g Liver	Kidney	4 hours, mg As/g Liver	Kidney
5% soil 1	450	0.87±0.26	0.89±0.17	1.23/1.24	1.85/1.28
16% soil 1	1350	2.7±1.2	2.7±1.1	-	-
10% soil 2	110	0.95±0.14	0.89±0.10	1.64/1.92	1.76/1.85
10% soil 3	120	2.9±0.24	2.32±0.38	2.4/2.0	2.3/-
No soil	0	0.14±0.06	0.14±0.07	0.18/0.12	0.35/0.16
^{74}As-arsenate (N=5)	120	5.1±1.2	4.0±0.5	3.5/1.0	3.1±0.8

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The Application of Risk Assessment Techniques to the Investigation and Exhumation of a Former Burial Ground.

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Abstract

Current UK guidance and other reference documents are mainly directed for use on sites contaminated by previous industrial uses, and typically address contaminants such as metals and hydrocarbons. The major hazards associated with the potential contamination of soils and / or groundwater from the burial of human remains incubating communicable diseases (e.g. pathogens and bacterial infections) are less well-documented and rarely applicable to redevelopment projects.

The need for a detailed site-specific risk assessment is of primary importance if proposed exhumations of such remains are considered to be satisfactory with regard to human health (both on and off site) and the environment. Qualitative risk assessment techniques developed from contaminated land projects were applied to protect workers and the general public during the investigation, excavation (exhumation) and reinstatement of a former Infirmary burial ground in Newcastle.

Forward - Client Overview

The £54 million International Centre for Life, Newcastle Upon Tyne is the North-east of England's principal Millennium project and forms one of the nations twelve flagship Millennium developments. It will be based upon the discovery of the structure of DNA by Crick and Watson in 1953 and the increasing significance of the subject of Genetics to all our lives.

The development comprises The Genetics Institute, The Bio-Science Centre and The Helix visitor attraction designed to accommodate up to 400,000 visitors a year. All elements of the development are now under construction and at the time of drafting, on programme and within budget. This has only been possible due to the works and approach described which lead to the timely removal of a fundamental site constraint – some 700 human burials from across the site.

As Agent to The International Centre for Life Trust, the TWDC commissioned a desk study and environmental site investigation to ensure the necessary early progress of the project was achieved. The desk study identified the potential existence of a burial ground associated with the former Newcastle Infirmary. Although identified, the potential significance of this constraint was not initially recognised in terms of either design, programme or budget.

The technical approach proposed by Mott MacDonald Ltd and adopted by the team is described in this paper. From the Clients' point of view it provided a clear, familiar and structured approach to the investigation, clearance and subsequent development of the site. It also integrated well with the adoption of CDM Regulations on the site.

The site investigation undertaken by Mott MacDonald Ltd confirmed the existence of the burial ground. As the investigation progressed it became clear that an extensive and thorough clearance of the whole site would be required, not only the area of the recorded burial ground. It was also apparent that the remains represented a unique opportunity to study early medical techniques as practised on the poorer members of society in the eighteenth and nineteenth centuries. For these reasons the Client decided to proceed with a closely managed *scientific* rather than *commercial* clearance of the human remains.

However, there were two areas where the investigation and subsequent clearance works proved problematic:

1. the public (or rather media) perception of the work being undertaken; and
2. the associated lack of understanding and inappropriate reaction of some funding partners.

Contaminated Soil '98, Thomas Telford, London, 1998, 331–336

For reasons of safety and human dignity our initial approach was to totally exclude the media. However, the high profile of the site, its location and a strong corporate history for active involvement of the media lead to a review and change in this approach. This lead to a period of significant and very intrusive media interest.

Having made strenuous efforts to ensure that a rigorous approach was adopted throughout the desk study, investigation and subsequent analysis of the burial ground and the recovered remains, it was disappointing to see the reaction of others involved in the projects, notably some of the funders. There appeared to be a misunderstanding of the approach adopted and its rigour, and consequently an over-reaction as to the potential future consequences. This must in part be the responsibility of the project team for not successfully explaining their methods and approach.

The identification, investigation and clearance of the burial ground associated with the former Newcastle Infirmary has been achieved on time and within budget. This in turn has enabled the International Centre for Life project to proceed to programme. It has been achieved by the very successful collaboration of a unique specialist team that provided excellent managed and recorded works, which are proving to be a considerable value.

Cliff Jessett, TWDC

Background

The site under consideration forms part of the Tyne and Wear Development Corporation Millennium project entitled "The International Centre for Life". The site is located adjacent to central railway station within the heart of Newcastle City Centre.

Immediately prior to establishment, the site comprised a number of different land uses including a bus garage, to the north of Scotswood Road, a car park, a garage and a children's playground. There was also a substantial area of derelict land, mainly rough grass and demolition rubble, located to the southern quarter of the site, adjacent to Forth Street.

A public footpath and the station to the east, Scotswood Road to the north, Railway Street to the west and Forth Street to the south formed the immediate site boundaries.

Historically, the whole site was a compilation of smaller sites with various industrial uses, including Abattoirs/Cattle Markets, a Wire Works and localised areas of landfill (part of a former stream) and included an Infirmary on part of the site.

As with all potentially contaminated land investigations, the first step was to determine the site history and land uses and to establish the likelihood of contamination. In particular, specific information was required with regard to the nature of the former Infirmary.

Hazard Identification – Stage 1 Desk Study

Mott MacDonald undertook a comprehensive Stage 1 desk study contamination review in September 1996 which incorporated an assessment of all available information. The desk study included the following:

Table 1
Summary of potential hazards arising from former uses, Desk Study Contamination Review

Period of use	Former use	Desk study findings	Potential hazard(s)
1749	Skinner Burn (northern) a former watercourse - infilled and possibly culverted	Made ground (2.5m) Hydrocarbon (engine oil / coal tar) contamination	Made Ground Hydrocarbon contamination
1751-1906	Newcastle Infirmary Main buildings demolished 1954	Burial ground operational between 1753-1845 (closed 1835-38). Suspect between 450-700 burials. Burials reportedly "removed" 1852-53 (unsubstantiated but possibly to charnel pits).	• Infectious diseases • Weil's disease • Lead poisoning
1753/ 1761	Coal borings	Coal seams reportedly at 20-25m and 60m bgl. 1947 is last date of possible underground working. Disused mine entry shaft on-site (status uknown).	• Subsidence • Contamination from coal workings
1830-1864?	Cattle Market	No records of burial sites for diseased animals on-site.	Pathogens
1849/ 1859	Skinner Burn (southern) a former watercourse - infilled	Made ground (2.5m)	Made Ground
1878?-1930	Pig and Sheep Markets	No records of burial sites for diseased animals on-site.	Pathogens
1927-1954	Timber Merchant	No records of operations (located within southern Infirmary buildings)	Contamination from timber treatment (resins/adhesives, solvents, pigments/dyes, preservatives)
1954-1963	Abattoir and Lairs (western Infirmary buildings)	No records of burial sites for diseased animals on-site.	Pathogens
1930-1969?	Marlborough Crescent Bus Station	3no. fuel tanks c. 1931 (unknown status)	Contamination from vehicles (hydrocarbons)
1930-1992	NCP garage forecourt	3no. 3000g petrol tanks, 1no. 5000g petrol tank and 1no. oil tank plus fuel lines (status unknown) Hydrocarbon (diesel) contamination extending through made ground into glacial deposits.	Contamination from vehicles and fuel storage (hydrocarbons)
1947-1954	Sawmills and Wood Shavings, Marlborough Crescent	Hydrocarbon (engine oil / coal tar) contamination	Contamination (hydrocarbons, pigments / dyes, coatings, solvents)
1947-1969	Sawmills and Wood Shavings, Forth Street	Hydrocarbon (engine oil / coal tar) contamination	Contaminants (hydrocarbons, pigments / dyes, coatings, solvents)

1. a review of historical map information;
2. a review of geological, hydrological and hydrogeological information;
3. consultation with regulatory authorities;
4. a site inspection; and
5. a review of previous reports.

The findings of the contamination review are summarised in Table 1.

From the desk study it was concluded that further information was required on the following:

1. the fuel tanks associated with the bus station;
2. the fuel tanks and supply lines associated with the Garage;
3. the contamination associated with the timber and sawmill industry uses; and
4. *the extent and status of the former Newcastle Infirmary burial ground.*

This paper looks at the way in which qualitative risk assessment techniques, developed primarily for contaminated land investigations, were applied to the investigation and exhumation of human remains associated with the former Newcastle Infirmary burial ground. For the purposes of this paper, other contamination issues associated with the site are not discussed in detail.

Archaeological Desk Study Findings

The archaeological desktop study undertaken by Newcastle City Archaeology Unit collated general information on the history of the Newcastle Infirmary and the associated burial site. This archaeological information formed the basis of the environmental/contamination site investigation design for the burial ground.

Newcastle Infirmary was opened in 1753, and the Infirmary chapel and burial ground were consecrated in the same year. Records indicate that the infirmary was a product of "the Age of Philanthropy", a movement in the early 18th Century, which set up subscription hospitals to provide public health care for the poor. The infirmary's work was both curative and instructive, the patients were not simply to be cured, they were also to be used to advance medical knowledge.

Generally the infectious and incurable were not admitted[1]. Records indicated that the Infirmary governors decided in 1774 to exclude all fever cases. However, it was not possible to ascertain how far these rules were applied and it is possible that the admittance of patients dying of other disorders may have been incubating more serious diseases. In 1801, governors planned to establish a fever ward to accommodate cases arising whilst as inmates of the Infirmary. However, it was suspected that fever patients were to be admitted from elsewhere and subsequent public complaints prevented the admittance of any fever patients to the new ward.

The burial ground was in use by the Infirmary between 1753 to 1845. The grounds were closed temporarily between 1835 and 1838, possibly due to overcrowding. Burial Records survive for the years 1803-1815, when there were 159 interments, and 1822-1845, when there were 270 interments. There are also Admissions Registers for the Infirmary for the period 1778-1788, which state whether the patient was discharged as "cured" or "dead". During this period 359 inmates were discharged as "dead", but what was not clear was whether they were buried within the Infirmary grounds.

In 1851, six years after its closure, the burial ground land was lost when a new Infirmary wing was constructed. The archaeologists reported that Infirmary records for this period were "*conspicuously uninformative*" with regard to the details of the burial ground overbuilding and there was no information on whether all or any of the bodies were removed during these works. This intimated the potential for charnel pits on the site.

From the variety of information obtained during the archaeological desktop study, it was predicted that the total cemetery population could be between 500-1000. The number of burials which may subsequently have been truncated, disturbed or removed during the building of the wing, or other later development (e.g. Air Raid Control Centre 1940-45),

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[1] Patients reported to be specifically excluded from treatment were pregnant women, children under 7 years old, the insane, sufferers from measles, smallpox, infectious fevers, incurable cancer, highly developed scrofula, consumption, hectic fever dropsy, palsy.

could not be ascertained. Nor was there any up-to-date information to confirm that any burials were present at all. (For all intents and purposes, the site was a car park for station commuters.)

Although not a fever hospital, records showed that it had had a number of patients die from a variety of infectious diseases from 1745 through to the mid nineteenth century. Records indicated the possibility that such patients had been buried on site. What the records did not show was:

a. the "mode" in which the deceased had been buried, i.e. whether in wooden coffins, shrouds or lead lined coffins etc. nor

b. the "manner" such as single graves, side by side and/or stacked graves etc.

All of which would brought specific potential risks to site workers during actual exhumation and removal from site.

Burial Ground Site Investigation - Design and Qualitative Risk Assessment:

The design of the Stage 2 site investigation (burial ground) had to satisfy environmental, geotechnical and archaeological investigation objectives whilst meeting qualitative risk assessment judgements and health and safety requirements.

From the desk study, the main hazards identified as being associated with the Infirmary burial ground included: lead, infectious body liquor, tetanus, tuberculosis, smallpox, and Weil's disease. The location of a former abattoir/lair within the hospital buildings also added the potential for two further biological hazards to be present: parasites and anthrax.

From the information supplied by Health and Safety Executive in their document the Infectious Hazards of Human Cadavers, it was decided to compile a qualitative risk assessment which strictly followed the procedures for a best practice health and safety risk assessment. Although by its nature such a risk assessment follows more stringent target scenarios than that employed for the majority of contaminated land projects, the burial status of the cadavers was unknown and should any of them have been incarcerated in lead lined coffins then the potential existed for infectious diseases to have remained within the body liquor which would have been held within the coffin, thereby categorising all potential sources within the model as HIGH risk.

Further within the source-pathway-target model the traditional pathways to the targets were clearly identified by medical advice, but definitive information on the half-life of these diseases within soil was not available. This matter was heightened at the time by the reporting of human health problems associated with anthrax from a former abattoir site in the Wiltshire area. As previously stated historic maps for this site indicated that abattoirs had also been in operation close to the burial area. Thus the risk model had an above average number of potential pathways opened, although these were subsequently kept under review during the investigation and actual works (see Table 2).

Table 2

Source Pathway Target Model (Desk Study) for Burial Ground - based on short term considerations for soil contamination during Site Investigation

	Type of Hazard					Plausible Pathways							Level of Risk			
Potential Contaminant	Toxic	Phyto-toxic	Carcino-genic	Corrosive	Combus-tible	Ingestion	Inhalation	Dermal Contact	Root Uptake	Physical Transport	Groundwater Movement	Direct Movement	Humans	Surface Water	Ground water	Buildings/ Building Services
Pathogen	High	Low	Low	Low	Low	Yes e.g. soil	Yes e.g. dust	Yes e.g. cuts	No	Yes e.g. wind	No	Yes e.g. Grave Robbers	High	Low	Low	Low

The clearest targets were not only those working on the site during the investigation and subsequent exhumation but children at an adjacent school play area. Potential carriers of the diseases existed in the form of rodents and other small mammals. An added complication to the target modelling was the potential for grave robbers. Under advice from the Newcastle Environmental Health Dept. it became apparent that the act of grave robbing is still prevalent in the United Kingdom. Therefore although as will described later security was effected immediately to prevent such a situation, in the model the grave robbers became not only a target but also a potential pathway for spreading disease to the general public.

From the above it was decided to categorise the site as a "RED" site in accordance with the criteria specified in the British Drilling Association manual for the Site Investigation of Potentially Contaminated Sites. For practical purposes, it was decided to use these criteria as they are generally understood by all persons and organisations that regularly undertake site investigations. Further, and as a supplemental operation to the risk assessment a flow chart was compiled which ensured the safe movement of exhumed remains from burial ground into dirty and clean safe room areas (before movement by licensed carriers from site) by suitably protected operatives, and the movement in and out of the works by the workforce via the decontamination unit. The practical application of this flow chart will be described later.

The site investigation was undertaken in close collaborations with the Newcastle City archaeologists, the Environment Agency, Newcastle Environmental Health Dept., the Health and Safety executive and the Newcastle General Hospital Occupational Health Unit (NGHOHU). These organisations gave advice on all items relating to the working practices and monitoring of site workers and visitors during both the investigation and subsequent exhumations.

The monitoring regime for the site workers was compiled by NGHOHU, with procedures established for rapid response site attendance by suitably qualified medical staff should any of the workers start to exhibit signs of distress. It was agreed that blood samples should be taken from all those visiting the works, and at regular intervals throughout the operation for those working on site. However little guidance could be given as to the period thereafter that monitoring could / should continue for the site workers and it was finally decided to cease monitoring once the exhumations were complete, with all site workers being advised to contact their own General Practitioner so that suitable notes could be placed upon their files. This matter raised however the fundamental question for the Client, at what point did his responsibility for ensuring the health and safety of the workers end and it was finally agreed that due to the control standards set on site, if no person exhibited any signs of distress within the period that the samples were retained by NGHOHU then the Client could be seen to have taken all reasonable care in the discharge of his responsibilities. However no HSE risk assessment procedure is in place to ensure conformity of discharge of this duty across the whole range of contaminated land type commissions.

A key part of the design of the site investigation was the translation of the flow chart into the actual provision of adequate site management facilities, including the site security, to prevent spread of potential contaminants. Access to the burial ground area was a key issue, and it was decided to follow the criteria set up in the nuclear industry of having all site worker social/living facilities outside of the main works compound This ensured that control of such items as used/dirty environmental protective clothing became part of the site waste management operation controlled by a licensed organisation. Further it enabled others visiting the site, and having no involvement with that part of the works to move about unhindered and in safety.

As there were potential problems associated with trespassing onto the site, as well as considerable media interest both in this major city centre scheme and the specific burial removal operation, an outer security system was established with patrols on site 24 hours a day.

In line with the risk assessment flow chart access for both personnel and plant/machinery was designed to be through a clean/dirty corridor in order to minimise the potential for cross contamination. Working practices on-site were designed to minimise exposure to contaminants, which included maximum working times inside the burial area. Additional protection of workers on-site was also provided through the provision of PPE as specified for "red" sites and on-site medical facilities were provided supported by NGHOHU.

Additional requirement of the authorities for visual protection and low-level dust control were provided by the design of an environmentally secure inner fencing system. The fencing system was based on the specification compiled by Mott MacDonald for use on city centre Gasworks sites, but due to the exposed nature of the site and the fact that the works were being undertaken during the months when high winds could be expected the low-level dust control was included not only as a precaution but as an environmental control mechanism capable of audit. The exhumations were to be undertaken under polythene tunnels, thus the highest degree of risk for air borne contamination was during the site investigation when remains unearthed would be open to air.

As a risk assessment exercise this commission highlighted the volume of knowledge in the public domain about specific matters associated with communicable diseases, but the information was usually presented in a stand alone quantitative form, a great deal of which it was difficult to assimilate into a common base without automatically reverting to a worst case scenario when compiling the qualitative risk model. Considering the quantum of expertise they could consult on communicable diseases the authors were surprised how often they had to resort to use of their own practical professional judgement rather than previous case study experience.

Findings and Risk Evaluation:

It was agreed with the archaeologists that the site investigation would be undertaken by using a grid of crossing trenches, taken down in 225-300mm layers, and generally stopped once the top of the burial remains were intersected (around 1.76m bgl). The extent of the burials were found to conform to the boundaries of the burial ground derived from the archive plans. The investigation recorded 43 articulated burials, most of which were embedded in soil. 12 bodies were lifted at chosen locations during the site investigation, to sample the depth of burials and the preservation of bone. Based on

site investigation findings, it was estimated that the surviving cemetery population was in the region of 700 articulated burials, and an unquantifiable amount of disturbed human bone (present in the surrounding cemetery soil).

Outside the burial ground, bone deposits were found in an additional archaeological investigation trench originally positioned to investigate the infilled Skinner Burn watercourse. The remains wee not found to be in-situ burials, and appeared to have been deposited in a channel pit. Further investigation of the remains by the on-site osteologist revealed that many of these remains were comprised of autopsied and/or dissected cadavers. Further outlying bone deposits comprised trial pit spoil (from an early geotechnical investigation) and a small pit of amputated limbs. Stray skeletal material was proposed to be cleared by a machine 'sweep' of the area south of the Infirmary remains.

During the site investigation, soils obtained from the archaeological trenches were analysed for a range of contaminants, mainly general suite. Additional testing was also undertaken for anthrax in the vicinity of the former abattoir. Sampling for pathogens (specifically smallpox) was not able to be undertaken, either because the service was not available (smallpox analysis is not undertaken in the UK) or turnaround times were impractical (TB samples were obtained[2] but results were not available for three months). In most instances, microbiological sampling was just not available at a reasonable cost, or within a practical timescale. Anthrax was the only exception to this. Hence, it was decided at the design stage to place a greater emphasis on protection from PPE for site workers.

The findings from the site investigation indicated that although the conditions on-site were conducive to the preservation of a number of soft tissue types and products of decomposition, no skin or muscle tissue was recovered during the site investigation, thereby reducing the survival chances of pathogens as well as the transmission hazards.

Once the site investigation had been completed and laboratory results available a full Source-Pathway-Target Qualitative Risk Assessment was undertaken to ascertain the degree of Risk associated with all general contaminants and anthrax analysed during the site investigation. This combined with the status of the burials (i.e. mainly earthbound skeletal material) was the most important outcome from the investigation and subsequent risk assessment. It enabled the designers to demonstrate to the Regulators that the burial ground could be reduced in status from "Red" to "Yellow". This not only reduced site running costs but could also enable more specific programming of the exhumation process.

Burial Ground Removal - Excavation / Exhumation:

Once the site investigation had been completed, a decision had to be made by the client on the type of clearance of the burial ground, i.e. scientific or commercial. The arguments for a scientific removal included the importance of the anthropological material with regard to date, class and region, as well as the evidence for medical interference with cadavers. The implications of a commercial clearance would mean the wholesale removal of earth and bones, more than likely to a landfill site. The obvious benefits for commercial clearance, however, were those of cost and timescale. The client explains how the decision was reached in the attached forward to this paper.

A team of 10 archaeologists undertook the exhumation process under the supervision and monitoring of Mott MacDonald. Further soil samples were taken during the course of the works with subsequent laboratory testing being directed to towards the contaminants highlighted during the site investigation. Each set of remains were carefully exposed (under polythene tented structures, to reduce the potential spread of airborne particles and for protection of the dig) with photographs and notes and sketch recording of the find. Each set of remains were then taken through the dirty room, specifically tagged if of specific archaeological interest and then securely stored on site.

Throughout the investigation and exhumation the operation was independently assessed and reviewed by the projects' CDM Planning Supervisor to ensure that the agreed chain of custody procedures were followed, with close liaison being maintained with the Environmental Health Department. The remains that were exhumed were of particular interest to archaeologists who specialise in eighteenth century diseases and surgical techniques, and following discussions with the Home Office it was agreed that the remains would be initially stored at Sheffield University (for further examination) before being reinterred at a location to be agreed with Newcastle Council officials.

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[2] The analysis involved the demonstration of lipids specific to Mycobacterium tuberculosis.

POLLUTION-INDUCED COMMUNITY TOLERANCE IN TERRESTRIAL MICROBIAL COMMUNITIES

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Key words: Metal, field experiment, zinc, contaminated soil, ecosystems, ecological effects, micro-organisms, microbial activities, bacteria

SUMMARY

The concept of pollution-induced community tolerance (PICT) has been used to demonstrate effects of heavy metals at a contaminated site at Budel (The Netherlands) on the indigenous microbial community present in the soil. The method was based on the use of multiwell plates (Biolog®) for producing concentration versus effect relationships of 95 different microbial metabolic activities. For this, artificial exposure in the multiwell plate was established to the contaminant supposedly causing toxic effects in the field; zinc. There was a clear relationship between the sensitivity of the microbial communities extracted from the soil for zinc and the level of zinc contamination in the field in the range of 16 to 360 mg zinc per kg DW soil.

Contaminated Soil '98, Thomas Telford, London, 1998, 337–343

INTRODUCTION

In ecotoxicology it is still a challenge to prove toxic effects of a contaminant in the field on ecosystem structure and functioning. Scatter, natural variability and the impact of other factors often confuse the effects of contaminants, especially at concentrations in the range of environmental quality objectives set for protecting ecosystems. In order to tackle this problem, it has been proposed (Blanck et al, 1988) to study pollution-induced community tolerance (PICT) as an expression of toxic damage at the community level of ecosystems (Fig. 1). The concept of PICT encompasses the phenomenon that toxic effects reduce the survival of the most sensitive organisms within a population, thus increasing the net tolerance of the community. Inversely, tolerance of the community for a contaminant is a strong indicator for the presence of that contaminant.

The issue of causality is embedded in the concept, essentially by performing concentration versus effect studies under controlled conditions in the laboratory with the chemical that is supposedly causing toxic damage on the microbial communities collected at contaminated sites. This yields observations on sensitivity differences under laboratory conditions that are indicative of differences in the field.

The ecological relevance of sensitivity loss in communities has been well established. For instance Millward and Grant (1995) demonstrated the PICT for copper with nematodes to be concordant with nematode community structure and a depauperated species abundance. Furthermore Doelman et al. (1994) related loss of sensitivity for heavy metals in bacterial populations to a decreased metabolic versatility, i.e. resistant bacteria did not degrade as much organic substances as their sensitive counterparts.

This paper describes the application of a method previously published (Rutgers et al, accepted) for determining PICT in terrestrial microbial communities by use of an automated multiwell plate system. Microbial communities extracted from topsoil of a heavy-metal contaminated area nearby a zinc smelter were investigated.

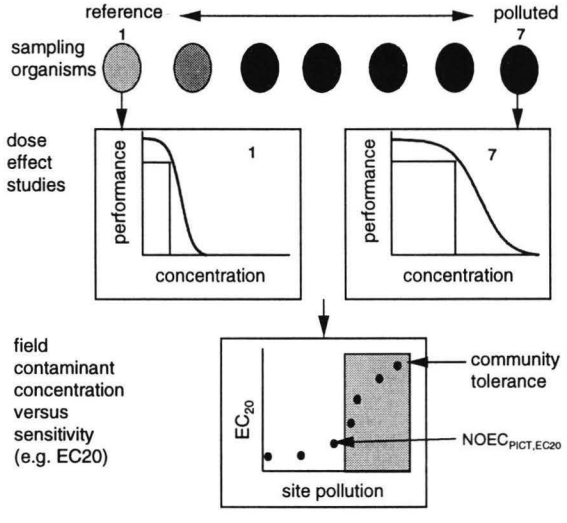

Figure 1. *Schematic representation of the experiment for determination of pollution-induced community tolerance (PICT) (redrawn from Posthuma 1997).*

MATERIALS AND METHODS

March 27, 1997 five sandy soil samples were collected from the upper mineral layer (2 - 7 cm depth) from spots at 1, 2, 6, 14, and 20 km distance from a zinc smelter (Budel-Dorplein, The Netherlands) in North-East direction. The sample for each spot was composed of ten subsamples of approx. 50 g each from an area of 25 m^2 and collected in plastic bags. The soil was sieved (2 mm) and mixed and the five plastic bags were stored at 10°C for 14 days. The spots at 14 and 20 km distance from the zinc smelter were regarded as reference. Soil analysis showed that total zinc concentrations were 360, 104, 83, 35, and 16 mg zinc per kg DW soil, respectively. pH (KCl) was in the range of 2.7 to 3.8, and organic content and humidity were in the range of 5 to 13 %, and 10 to 22 %, respectively.

Extraction of microbes from the soil was performed by adding 5 g soil to 50 ml sterile buffer solution (1 mM bis-tris; pH 7) and shaking during 20 min at 150 rpm on a rotary shaker (30°C). The debris was precipitated by centrifugation at 500 g for 5 min. Subsequently the supernatant, containing microbes, was diluted (5 to 10 x) in eight solutions containing 0.01, 0.1, 1, 10, 100, 250, 1000, 2500 mg/l zinc (total concentrations as $ZnCl_2$) at pH 7. NaCl was added to the solutions at concentrations inversely related to the Zn concentrations in order to obtain comparable concentrations of Cl^- (for assigning the effects to the presence of zinc and not to increased salt levels).

Prefilled 96-well plates (GP Microplate™; Biolog, Hayward, CA, USA) were used for determining the relative sensitivity of the metabolic activities of the isolated micro-organisms of each field sample at the eight artificial exposure levels. Biolog® plates are prefilled with a dried mineral salts medium, a tetrazolium dye, and 95 (1 blank) different substrates such as carbohydrates, polymers, aromatic structures, amino acids, etc. Although essentially developed for the identification of bacterial isolates, these plates are increasingly being used in ecological studies (Insam, 1997). In environmental studies, the conversion of a compound in the Biolog plate is considered to represent activity of the microbial community.

The method is decribed in more detail in a previously published paper (Rutgers et al, accepted) The multiwell plates were inoculated (150 µl per well) with the zinc solutions (0.01-2500 mg/l) containing the extracted micro-organisms from the soil communities. Within this experimental setting, some precipitation of zinc was observed due to the presence of phosphate buffer. The amount of free aqueous zinc was calculated to be approximately 20%, as confirmed by Zn measurements of filtered solutions from the multiwell plates after the incubations. The plates were incubated for 10 days at 28°C. Every 12 hours the absorbance at 590 nm (A_{590}) of each well was determined by a microplate reader-spectrophotometer. Positive colour development in the wells was defined as an increase of A_{590} over 0.5 units above background level. The rate of colour development over time intervals of 12 hours for each individual well was calculated from the A_{590} values. The highest rate of colour development was regarded as the activity of the microbial inoculum for the respective substrate in the well.

For each of the five original field samples we thus obtained microbial activities for many (maximally 95) substrates at eight artificial zinc concentrations in the multiwell plates. The data were ordered so as to construct (artificial) zinc concentration versus activity relationships for each substrate and field sample. The data (for each relationship separately) were fitted to a sigmoid curve according to the model of Haanstra et al. (1985) using statistic software (Graphpad Prism™, San Diego, CA, USA). The relative

sensitivities of the isolated micro-organisms for artificial zinc exposure (EC_{50}^{BIOLOG}; the concentration of zinc causing 50% decrease in activity in comparison to its non-treated control in the multiwell plate) were calculated from the relationships.

RESULTS AND DISCUSSION

Colour development in Biolog® plates after inoculation of microbial communities extracted from soil samples is dependent on inoculum density. With the inoculum density used in this study (approximately 1×10^3 to 5×10^3 colony forming units per well) colour development was observed in typically 78 to 89 wells.

The rate of colour development decreased with increasing artificial zinc concentration, and consequently, 78 to 89 different EC_{50}^{BIOLOG} values could be calculated from the concentration versus activity relationships of the positive wells.

The microbes in extracts from the various soil samples showed EC_{50}^{BIOLOG} values ranging from 0.1 to over 2500 mg Zn l^{-1}. In Fig. 2 a typical example (α-D-glucose) of EC_{50}^{BIOLOG} values of the different soil microbial communities around the smelter is presented. In this selected example the PICT is convincingly demonstrated as an increased EC_{50}^{BIOLOG} value. EC_{50}^{BIOLOG} values are based on added zinc in the multiwell plate; the free zinc concentration was approximately 20% of the total zinc concentration, and therefore the EC_{50} based on 'available' zinc was estimated to be 20% for all substrates. For the determination of PICT this was not a serious problem, because the sensitivities were interpreted in a relative way, namely: did field exposure affect EC_{50}^{BIOLOG} differently in low- and high exposed plots? In some cases, the artificial zinc exposure in the multiwell plate had no serious effect on the colour development. In these cases the EC_{50}^{BIOLOG} of the respective microbial activity was regarded to be over 2500 mg zinc l^{-1}, arbitrarily.

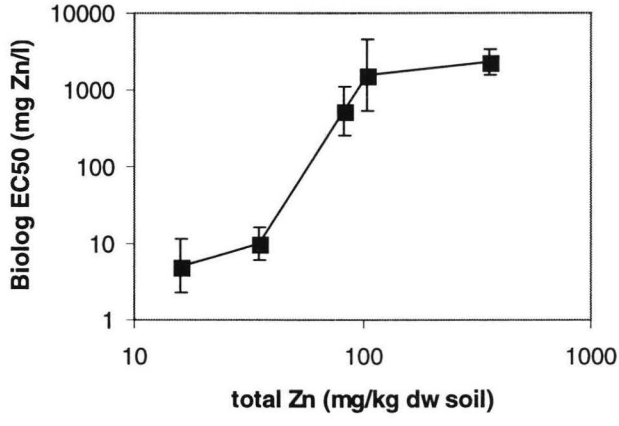

Figure 2. *Typical example of* EC_{50}^{BIOLOG} *values of one microbial activity (α-D-glucose) of microbial communities around a zinc smelter in Budel. The* EC_{50}^{BIOLOG} *values are plotted as a function of the total field concentration of zinc (mg zinc kg dw soil*$^{-1}$*). Error bars indicate 95% confidence intervals.*

78-89 EC_{50}^{BIOLOG} values of each extracted soil microbial community were plotted in cumulative frequency distribution curves (Fig. 3). The EC_{50}^{BIOLOG} values over 2500 mg zinc l^{-1} have been taken into account but were not drawn. The resulting curves demonstrated a sigmoidal-shaped distribution of EC_{50}^{BIOLOG} values for each spot. The microbial community of the reference spots (at 14 and 20 km distance from the zinc smelter) demonstrated the highest numbers of sensitive activities; the median of the sensitivities (the median of 78 - 89 values) were 35 and 16 mg zinc l^{-1}, respectively. The microbial communities extracted from the soil with elevated zinc levels (at 1 and 2 km distance form the zinc smelter) demonstrated significantly higher EC_{50}^{BIOLOG} values. For instance, at 1 km distance of the zinc smelter the extracted community had an median EC_{50}^{BIOLOG} value of 1216 mg zinc l^{-1}.

These observations confirmed the hypothesis that exposure of soil microbial communities to zinc resulted in the loss of sensitivity, possibly by loss of some sensitive microbial activities. Consequently application of the PICT concept can be a valuable tool to detect effects of zinc under field conditions.

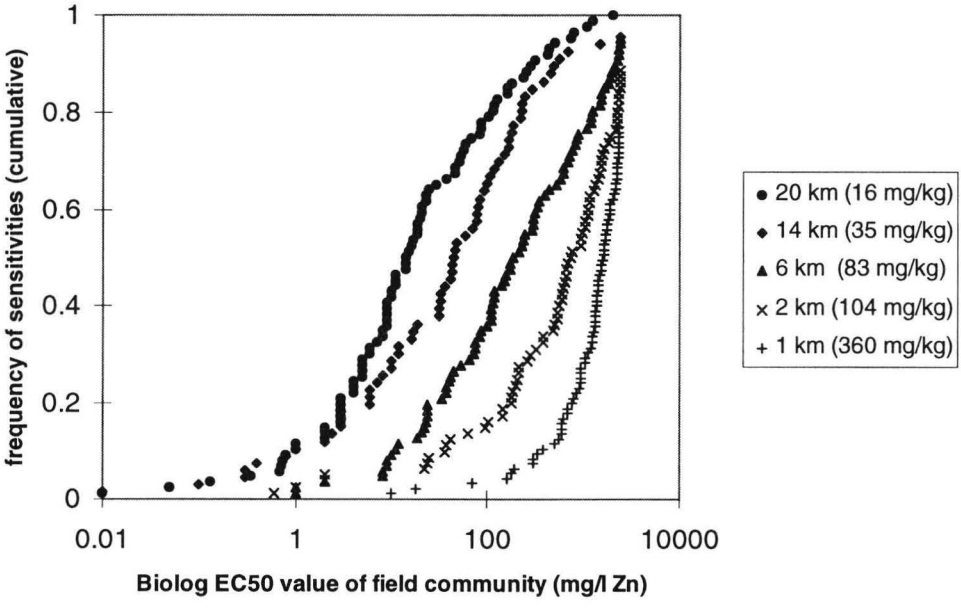

Figure 3. *Cumulative frequency of* EC_{50}^{BIOLOG} *of microbial activities around a zinc smelter near Budel. The figure shows* EC_{50}^{BIOLOG} *values for each positive Biolog substrate (78 - 89) and 5 different field communities* (●,◆,▲,×,+) *with various levels of exposure. The distance to the zinc smelter (in km) and the contamination level are given (between brackets: total zinc concentration in mg zinc per kg DW soil).*

Furthermore, the range of sensitivities seemed to be broader for the non-exposed field communities compared to the high-exposed field communities; the slope of the distribution curve is lower for the non-exposed community compared to the exposed community (Fig. 3). The possibility of an artefact could not be ruled out due to the inability to determine accurate EC_{50}^{BIOLOG} values over 2500 mg zinc l^{-1} within this experimental setting. Nevertheless, a small range of sensitivities in high-exposed communities is in line with the hypothesis of the loss of sensitive features, and the idea that toxic stress may reduce ecological versatility (Ernst, 1983).

Only a very small part of the total soil microbial community (Díaz-Ravina and Bååth, 1996) can be extracted and cultivated. Consequently, the outcome of the PICT experiment is valid only for the corresponding part of the community. Experiments with the unculturable part of the soil microbial community are difficult. Methodologically, our conclusion on the occurrence of PICT for zinc should be reinforced by an additional observation made on organisms collected with a significantly different extraction technique.

The presence of PICT can be considered as a strong indication for true toxic effects on organisms under field conditions, in the case of Budel in microbial communities exposed for 100 years to zinc. This is in itself a valuable observation, since classical observations on toxic effects on field organisms, such as population size or species richness, are often difficult to interpret due to unexplained variation and unclear causality. In addition to these advantages, other authors have explicitly mentioned another advantage of the PICT concept. Doelman et al (1994), for example, suggested that the net increase of tolerance of a community could be accompanied by a loss of metabolic functions. Although the metabolic functions studied in the present work do not necessarily represent relevant metabolic functions for micro-organisms in the field, the combination of the PICT-concept with the technique of multiwell plates offers great possibilities for studying change of ecological functions in stressed communities of soil microbes. Improving the ecological relevance beyond the mere observation that PICT occurs at a site with the aspect of ecological functions can be possibly obtained by analysing the field-relevance of the various substrates. In view of the findings of Doelman et al (1994), metal resistance is thus an undesirable phenomenon when quality of the environment and 'ecosystem health' are considered (Van Beelen and Doelman, 1997).

The demonstration of field effects of contaminants per se is relevant for site specific risk assessments and for the evaluation of the accuracy of environmental quality criteria - which are aimed at protecting against true effects of toxicants. In the present study, this is illustrated by the finding that the observed field effects (i.e. change of sensitivity; see Fig. 3) were present at the Dutch so-called target and intervention values. The intervention level is being used as trigger for (bio)remediation urgency; i.e. there is reason for clean-up investigations. The target value is regarded as a treshold for 'clean' soil. The site specific target and intervention value (i.e. after correction for organic matter and lutum content) are 61 and 312 mg zinc kg dw soil, respectively.

In summary, application of Biolog plates in the PICT method can asses the effect of contaminants on the functioning of microbial communities, because substrate utilisation patterns and sensitivities of an high number of functions can be determined. For instance, Lehman et al (1997) demonstrated effects of metal contamination on substrate utilisation profiles of microbial communities determined in Biolog plates and concluded

that it is an useful approach to evaluate ecological risks due to the presence of contaminants. Compared to classical biodiversity studies, the use of multiwell plates for micro-organisms is time- and cost-effective. As Biolog plates are not designed to characterise soil microbial communities, optimisation of the method by use of a modified set of substrates in the plates as proposed by Insam (1997) is useful.

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Higher Plant Growth and Microbial Toxicity Tests for the Evaluation of the Ecotoxic Potential of Soils

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Key words: bioassays, ecotoxicological, phytotoxicity, microbiological parameters, soil

Summary

Bioassays provide direct evidence of ecological effects associated with soil pollution. They are complementary to conventional chemical analysis. The commonly practised test methods were developed to analyze the ecotoxic potential of chemicals added to a soils. In the present investigation, the use of higher plant growth and microbial tests for the characterization of the ecotoxic potential of polluted soils was evaluated. Fresh uncontaminated soils of different types and abiotic properties were used for the interpretation of test results.

Kurzfassung

Biologische Testmethoden sind geeignet, das ökotoxikologische Potential kontaminierter Böden zu ermitteln. Sie ergänzen damit chemische Untersuchungen. Etablierte ökotoxikologische Testverfahren für Böden wurden zur Chemikalienprüfung entwickelt. In der vorliegenden Arbeit untersuchten wir die Eignung des Pflanzenwachstumshemmtests und mikrobiologischer Tests zur Bewertung kontaminierter Böden. Frische, unbelastete Böden unterschiedlichen Typs und abiotischer Eigenschaften wurden zur Interpretation der Ergebnisse verwendet..

Resumé

Les methodes de teste biologique sont adaptes pour determiner le potentil éctoxicologique des sols contaminés. Elles complétent donc les analyses chimiques. Des fuscédes de test écotoxicologique ont eté developpés pour prouver l'effet écotoxique potentiels des pollutants additiones au soil. Dans l'étude ci-jointe nous avons analysé du test de phytotoxicité et des tests microbiologique pour l'évaluation des sols pollués. Des sols sains de différent types et aux proprietes abiotique ont eté utilisés pour l'interpreétation des résultats.

Contaminated Soil '98, Thomas Telford, London, 1998, 345–354

Introduction

Chemical analyses can only provide information on the presence, concentration and variability of specific contaminants in soils. They do not enable a sure prediction of harmful biological or ecological effects, since the biological availability of pollutants in soils can vary considerably depending on the chemical species and the environmental conditions. However, bioassays are able to complement chemical analyses by showing the integral ecotoxic effects of all contaminants in soils, including those not considered or detected in chemical analysis. The following areas are suitable for the application of bioassays (Kreysa and Wiesner 1995): (a) supplementary risk assessment for contaminated sites; (b) efficiency control of soil remediation processing; (c) evaluation of a possibly ecotoxic potential of treated soils as a prerequisite to their further use.

Existing biological test methods (bioassays) were developed to describe the ecotoxic potential of a test substance added to a soil. These methods may also be used with some modifications for the ecotoxicological characterization of soils. One of the main problems which must overcome in ecotoxicological testing of soils of unknown quality is the absence of real controls for the assessment of results. In chemical testing, soils are amended with pollutants and the results are compared with those of the uncontaminated controls.

The present was performed to evaluate the applicability and feasibility of existing bioassays which have been recommended by various international agencies or national authorities to assess the ecological risks of soil contamination. The bioassays examined are the terrestrial phytotoxicity test (higher plant growth test) and microbial activity tests (dehydrogenase activity, soil respiration, and nitrification). In addition to polluted soils, fresh uncontaminated soils of different types and nutrients status were used to assess the possible endpoints of soil contamination and to interprete the test results.

Materials and Methods

Soils

Twentyfour different soils and a pure coarse sand were used in this study. They rrepresent a broad range of environmental factors such as pollution level, soil type, soil horizon, fertility, texture, pH, humus and nitrogen content (Tab. 1). Soils showing very low organic carbon contents and/or low fertility (e.g. Ahe, C-horizons) were classified as inert soils.

Contaminated soils were sampled at polluted sites (CTNT1, SPAK, GB, ES, BF) or obtained from remediation firms. The latter samples where they were treated in a bioreactor (EPAK-soils), or with composting techniques (B52, 67, 96). Concentrations of pollutants are given in Tab. 2. With respect to low Corg and nutrient contents (P and K not shown in Table 1), EPAK3a,4a, and SPAK were classified as inert soils.

For phytotoxicity tests field moist samples prepared were screened through a 5 mm sieve and stored in a cellar at ~ 16 °C. Samoles for the microbial tests were sieved through a 2 mm sieve and stored at 4 °C.

Table 1: Chemical and physical properties of tested soils

Soil	Type (FAO)	pH	Corg	Nt	Texture		
					clay	silt	sand
	Horizon	($CaCl_2$)	(%)	(mg/g)	(%)	(%)	(%)
Contaminated soils							
B52	excavated soil	7.7	1.45	0.3	2.	1	97
B67	excavated soil	7.7	1.87	0.4	5	13	82
B96	excavated soil	6.9	2.40	1.2	3	7	90
BF	excavated soil	7.7	1.51	0.4	16	24	60
CTNT1a	Cambisol Ah	4.5	2.90	2.3	18	55	27
GB	Cambisol Ap	5.6	9.60	6.4	9	11	80
ES1	Anthrosol yAh1	7.6	2.76	0.6	4	10	86
ES2	Anthrosol yAh2	7.8	3.81	0.4	1	8	90
Contaminated inert soils							
EPAK3a	excavated soil	7.5	0.50	0.6	11	78	11
EPAK4a	excavated soil	7.8	0.80	0.4	13	35	52
SPAK	excavated soil	6.3	0.76	0.3	7	17	76
Uncontaminated inert soils							
EH2	Anthrosol C	7.9	0.19	0.1	1	2	97
Sand	....	8.0	0.04	0.1	1	2	97
BR1	Vertisol Cw	7.0	0.84	0.5	46	49	5
BR3	Podzol Ahe	3.4	0.20	0.03	1	8	91
EPAK1a	excavated soil	7.6	0.40	0.18	10	84	6
Uncontaminated soils							
EH1	Anthrosol Ah	7.4	2.63	2.0	8	10	82
BR2	Rendzina Ah	7.1	8.50	8.9	36	28	36
BR4	Vertisol Ap	7.4	1.90	1.9	41	54	4
BR5	Colluvium Ap	7.4	2.10	2.4	34	50	16
BR6	Chernozem Ap	6.3	1.30	1.5	20	78	2
LAC	Luvisol Ap	6.8	1.10	0.9	7	18	75
ADS	Luvisol Ap	7.4	1.50	1.3	8	21	71
LUFA	Cambisol Ap	5.6	2.50	2.1	7	16	77
CTNT0	Cambisol Ah	3.3	5.30	4.6	28	61	11

Table 2: Concentrations of pollutants of contaminated soils

Soil	Heavy metals (mg kg^{-1})						PAH	Mineral Oil	2,4,6-TNT
	Cd	Cr	Cu	Ni	Pb	Zn	(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})
Organic chemical contamination									
B52	ND	ND	ND	ND	ND	ND	10-30	9000	ND
B67	ND	ND	ND	ND	ND	ND	ND	2000	ND
B96	ND	ND	ND	ND	ND	ND	50	1300	ND
BF	<0.2	22	25	14	165	117	5.28	2300	ND
CTNT1a	0.8	19	102	29	254	875	18	ND	1600
EPAK3a	<0.01	ND	8.8	23	25	83	294	154	ND
EPAK4a	<0.01	ND	7.8	31	29	72	563	ND	ND
SPAK	<0.2	885	4.4	7.2	24	44	1102	204	ND
Heavy metal and organic contamination									
GB	67.4	441	703	72.9	1043	1830	4.73	ND	ND
ES1	3.3	35.3	684	72.4	1878	2200	39.18	ND	ND
ES2	<0.2	8.2	59.1	17.4	222	222.5	29.39	ND	ND

ND = not determined

Test procedures

Higher plant growth tests were performed according to ISO 11269-2 using *Avena sativa L.* (oat), *Lepidium sativum L.* (cress) and *Brassica rapa Metzg.* (turnip). A self watering system with glass fiber wicks was used for the irrigation of test plants (Gong et al. 1998). Fresh shoot biomass of seedlings was weighed 14 days after emergence of 5 seedlings. The experiments were carried out in a greenhouse. The temperature varied from 16 °C to 35 °C in summer. In winter, it was maintained at 20 ± 3 °C and additional lamps provided a 16 h photoperiod and a light intensity of 17000 lux.
Soil nitrification and soil respiration curves were measured according to the methods described in the MATS Guidelines (Torstensson 1993). Dehydrogenase activity (DHA) of soils was determined using INT as a substrate (DIN 19733-2). The following parameters were derived from the respiration curves: basal respiration (R_B), substrate induced respiration (R_S) the metabolic quotient (R_B/R_s) and the lag time (time from the addition of substrate until the begin of exponential growth). All tests were conducted with four replicates.

Results and discussion

The response of plants in uncontaminated soils clearly differed greatly (Table 3) depending on the Corg-content, pH and fertility. For instance, fresh biomass of turnip ranged from 0.26 to 0.38 g pot^{-1} in inert soils and up to 3.74 g pot^{-1} in the ADS soil. Inert soils generally showed lower biomass production than the uncontaminated topsoils (Ah,p-horizons). Turnip and cress plants did not germinate, or grew poorly in the acidic CTNTO and BR1.

The growth of cress and turnip was considerably inhibited in polluted soils whencompared with uncontaminated soils. Less significant differences were obtained using uncontaminated inert soils.Turnip and cress yields of the contaminated EPAK3a (0.36 g; 0.22 g), which was also classified as an inert soil, exceeded those of the EPAK1a soil (0.26 g; 0.17 g).

In contrast to turnip and cress the growth of oat was only slightly inhibited, if at all, in polluted soils. No differences were obtained between oat biomass in uncontaminated and contaminated inert soils

Furthermore, it should be stated that light intensity and temperature also influence the growth of test plants. As a rule, biomass was higher in summer than in winter (data not shown).

The results of the microbial activity tests are also presented in Table 3. Dehydrogenase activities (DHA), nitrification and respiration rates of uncontaminated soils varied considerably depending mainly on their pH and Corg contents. As a rule inert soils exhibited lower microbial acitvity than uncontaminated topsoils (Ah,p-horizons). The EPAK1a did not nitrify at all and the BR1 showed a nitrification rate of 0.01 ng NO_2-$Ng^{-1}min^{-1}$.

The DHA and respiration rates (R_B, R_S) of mineral oil contaminated soils B52, B67 and B96, which were treated in a composting bioremediation process, did not differ significantly from or were even much higher than those of uncontaminated soils.These results were probably due to addition of compost during bioremediation. BF was also heavily contaminated with mineral oil (see Table 2) but was sampled prior to any remediation action, showed lower DHA and respiration. Contrarily, nitrification rates of oil-contaminated soils were much lower than those of uncontaminated soils showing the inhibitive effect of mineral oil to nitrifiers.

GB, ES1 and ES2 were mainly contaminated with heavy metals and to a lower degree with PAHs. When compared to uncontaminated soils they showed lower DHA and substrate induced respiration (R_S) but effects on basal respiration (R_B) were not obvious. Nitrification was only reduced in ES1 and ES2, while GB still exhibited a nitrification rate of 2.75 ng NO_2-$Ng^{-1}min^{-1}$.

According to their abiotic properties, the PAH contaminated soils EPAK3a, 4a and SPAK were classified as inert soils. They did not show any nitrification. The respiration rates of the contaminated EPAK soils did not differ from those of the uncontaminated reference soil EPAK, which was sampled at the same location. Respiration rates of the SPAK soil were rather odd. They even exceeded those of the uncontaminated inert soils. The basal respiration (R_B) of the SPAK sample was distinctly higher than the substrate-induced respiration (R_S), indicating an adverse effect of PAHs on soil microorganisms.

As a result of the high TNT contamination (1600 mg kg^{-1}), CTNT1a did not show any nitrification and reduced respiration rates when compared with the uncontaminated reference soil CTNT0 collected at the same site.

It is generally accepted that increasing environmental stress often causes a reduction in soil microbial activities. Anderson (1994) reviewed the use of physiological quotients in describing the reactions of microbial communities to a changing environment. The metabolic quotient (qCO_2) is one of the most frequently used parameters. It is defined as the quotient of basal respiration (R_B) and microbial biomass carbon (C_{mic}). In this study we used the ratio Q_R of the basal respiration (R_B) to substrate induced respiration (R_S) instead of the metabolic quotient because R_S is equivalent to C_{mic} (see Anderson and Domsch 1978). Q_R ratios were calculated for all soils exept BR2 (see Table 3).

Hund and Schenk (1994) reported that Q_R decreased with the bioremediation process of a PAH contaminated soil, and a correlation coefficient of 0.991 was obtained between PAH-concentration and Q_R. Since the soils used in this study varied with their chemical species and concentrations of contaminants, no correlation analysis could be made to relate the effects with specific contaminants (e.g. heavy metals, mineral oil, PAH). However, the contaminated soils showed Q_R-values ranging from

Table 3. Experimental results of the early seedling growth of higher plants and microbial activity tests

Soil	fresh shoot biomass[a] (g)			DHA (μg INT g^{-1} soil h^{-1})[b]	Nitrification (ng NO_2-N min^{-1} g^{-1} soil)[b]	Respiration (μg CO_2 g^{-1} soil h^{-1})[b]		Q_R (R_B/R_S)	lag time (h)
	oat	cress	turnip			R_B	R_S		
Contaminated soils									
B52	0.69	0.08	0.17	13.3	0.56	5.23	13.9	0.38	18
B67	0.76	0.04	0.13	8.68	0.41	3.40	11.9	0.29	19
B96	0.96	0.12	0.21	21.6	0.09	9.36	12.3	0.76	>30
BF	0.44	0.09	0.07	1.74	0.25	3.48	8.05	0.43	20
CTNT1a	0.42	n.g.	0.01	ND	0.0	0.83	1.35	0.61	>70
GB	1.03	0.05	0.27	0.85	2.75	1.46	5.24	0.28	38
ES1	0.92	0.32	0.52	3.63	0.50	3.11	6.71	0.46	23
ES2	1.03	0.30	0.52	1.38	0.57	1.77	5.27	0.34	21
Contaminated inert soils									
EPAK3a	1.57	0.05	0.36	ND	0.0	1.01	1.73	0.58	47
EPAK4a	1.37	0.01	0.01	ND	0.0	0.54	0.65	0.83	25
SPAK	n.g.	n.g.	n.g.	ND	0.0	7.4	3.5	2.11	ND
Uncontaminated inert soils									
EH2	0.77	0.25	0.38	0.44	0.59	0.53	0.88	0.60	40
Sand	0.88	0.26	0.35	0.69	0.66	0.54	2.19	0.25	38
BR1	0.89	0.25	0.36	0.25	0.01	0.49	1.90	0.26	7.2
BR3	0.62	n.g.	n.g.	2.41	0.44	0.50	2.49	0.20	11
EPAK1a	0.73	0.17	0.26	ND	0.0	0.52	0.98	0.53	>120
Uncontaminated soils									
EH1	1.17	0.53	0.71	6.09	1.47	2.85	9.40	0.30	17
BR2	2.57	1.46	3.27	27.3	93.4	8.64	...[c]	...	<0.4
BR4	1.52	0.61	1.35	4.30	4.61	2.19	8.28	0.27	7
BR5	1.25	0.60	1.10	17.8	29.1	2.93	26.2	0.11	9
BR6	1.03	0.35	0.73	8.03	7.77	1.27	18.9	0.07	7
LAC	1.01	0.51	1.35	9.47	2.72	1.03	13.7	0.08	18
ADS	1.64	0.70	3.74	6.07	4.03	0.68	9.43	0.07	15
LUFA	0.83	0.75	1.38	ND	0.48	1.21	21	0.06	15
CTNT0	0.47	0.01	0.16	ND	0.80	2.82	17	0.16	ND

[a] Means of 4 replicates, 5 seedlings in each replicate. [b] Means of 3 replicates. [c] The potential respiration (SIR) was not able to be determined because the exponential growth started too soon after addition of glucose (lag time<0.4 h as shown above). n.g.: No seeds germinated; ND: not determined.

0.29 (B67) to 2.11 (SPAK), whereas uncontaminated soils exhibited much lower Q_R ratios ranging from 0.06 (LUFA) to 0.30 (EH1). Therefore, Q_R might be used as an indicator for soil contamination. Unfortunately, the latter is not true if inert soils are also considered. the latter is not strictly true. Uncontaminated inert soils showed Q_R ratios between 0.20 (BR 3) and 0.60 (EH2), whereas those of EPAK3a lay in the same range (see Table 3).

Some investigations found that the lag time is substantially prolonged in heavy metal contaminated soils (Nordgren et al. 1988, Vonk and Matla 1993). In this study, extended lag times (> 18 h) were observed for all contaminated soils but also in some of the uncontaminated inert soils (EH2, EPAK1a) and the pure sand.

The main problem in ecotoxicological testing of soils of unknown quality is the absence of real controls. Our microbial investigations showed that Q_R ratios and lag times may be used as indicators of soil contamination. Most contaminated soils showed Q_R ratios > 0.3 and lag times >20 h. As some of the uncontaminated soils especially the inert soils tested, showed prolonged lag times and raised Q_R ratios, it seems to be risky to distinguish contaminated soils from uncontaminated soils by using strict threshold values. The latter is also true for nitrification. Uncontaminated inert subsoils may also show extremely low nitrification if any at all.

Results obtained from higher plant growth test also showed the impossibility of using distinct biomass production values for the characterization of the phytotoxic potential of soils. This is mainly true because the growth of plants increased with increasing light intensity and temperature during the summer period. Moreover, biomass yields of test plants were the same or differed only slightly in contaminated and uncontaminated inert soils.

In order to overcome the problem of lacking controls, two strategies may be recommende. One is to compare the results of contaminated soils with an uncontaminated reference soil showing the same chemical and physical properties, excluding the pollutant concentration. These soils can be sampled at a nearby uncontaminated site.

In this study, the CTNTO and the EPAK1a served as reference soils. They both showed higher biomass yields, nitrification rates and lower Q_R rates than the contaminated CTNT1 and EPAK3a,4a soils, respectively.

In most cases it will be impossible to find uncontaminated references especially, if soils which were treated in a composting remediation process are to be evaluated. Here a second strategy, the mixture of contaminated soils with uncontaminated reference materials may be an appropriate tool. In our experiment, B67 and B52 were mixed with the LAC soil and the pure sand. 50 : 50 mixtures of both contaminated soils with LAC and sand caused no difference in the biomass production of turnip, compared with unamended soils (Table 4). This indicates the extreme phytotoxicity of both soils.

We are planning to continue with these experiments including plant growth and microbial activity tests (nitrification test). Certified reference soils as well as inert materials (e.g. sand) will be tested. The use of inert material may be advantageous to classify soils in terms of ecotoxicity hazard because this material will not interact with the pollutants present in the test sample.

Table 4: Influence of dilution on the phytotoxicity of two contaminated soils

Soil	Dry biomass of turnip (g)[+]
B67	0.027±0.005 a
B67 + LAC (1:1)	0.026±0.003 a
B67 + Sand (1:1)	0.027±0.004 a
B52	0.029±0.002 a
B52 + LAC (1:1)	0.022±0.005 a
B52 + Sand (1:1)	0.033±0.005 a
LAC (control)	0.139±0.006 c
Sand (blank)	0.057±0.003 b

[+] After 14-day seedling growth (n=4, 5 seedlings in each pot). Different letter indicates significantly different from each other at 0.1% level.

Conclusions

Cress and turnip showed a high sensitivity to organic pollutants and heavy metals whereas oat poorly reflected the phytotoxic potential of soils. However, the test plants were also sensitive to the physical and chemical properties of soils. When testing soils during different seasons temperature and light intensity may also affect the growth of plants. A suitable procedure to overcome these problems could be the use of mixtures of contaminated soils with uncontaminated reference materials.

Microbial parameters such as DHA and respiration are unsuitable for ecotoxicological assessment of soils. In contrast, nitrification seems to be a suitable parameter to indicate soil pollution. Nevertheless, uncontaminated, inert soils also showed poor or even no nitrification. In these cases it may be profitable to inocculate these soils with uncontaminated A-horizon material.

In addition to nitrification, the Q_R-ratio (quotient of basal respiration and substrate-induced respiration) as well as the lag time after substrate addition seem to be appropriate microbiological parameters for ecotoxicological testing of soils. It is recommended to use a battery of tests inlcuding microbial and phytotxicity tests because no single parameter can reflect the effects of soil contamination to the same extent

Acknowledgements

This work was supported by s the BMBF (Federal Ministry for Education, Science, Research and Technology) of the Federal Republic of Germany under Contract No.

FKZ 1491031. Dr. Gong was financed by a BMBF scholarship. Special thanks are devoted to Mrs. R. Seyed-Mansouri, R. See, and L. Kapitzki for their technical assistance. We greatly appreciate Umweltschutz Ost GmbH, DMT Essen and Standort GmbH for the provision of some contaminated soils.

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A PROCEDURE TO ASSESS CONTAMINATED SOIL ECOTOXICITY

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Key words : Contaminated soil, Toxicity, Genotoxicity, Bioassays.

SUMMARY

Two polluted soil samples were assessed for both acute (Microtox®, *Daphnia magna*, *Thamnocephalus platyurus*) and chronic (*Pseudokirchneriella subcapitata*) toxicity, as well as for genotoxicity (Mutatox®). Bioassays were performed on soil water leachates and on soil solvent extracts to characterize not only the water soluble pollutants but also to evaluate less soluble pollutants or bound to soil fractions.
Coupling water leaching and solvent extractions to acute, chronic and genotoxicity bioassays allows us to define a step by step procedure to characterise the ecotoxicological hazard of soils. This procedure helps in defining the mobility and identifying the nature of the pollutants responsible for the measured toxicity. It can be used (i) to identify the hazard, (ii) to classify soil hazards and in so doing to map contaminated sites qualitatively (locating more polluted areas), (iii) to monitor and judge treatment success, (iv) to control rehabilitated sites.

RESUME

Le danger écotoxique de deux terres contaminées a été évalué par des tests de toxicité aiguë ((Microtox®, *Daphnia magna*, *Thamnocephalus platyurus)*, chronique (*Pseudokirchneriella subcapitata*) et un test de mutagenèse (Mutatox®). Ces tests ont été réalisés d'une part sur les lixiviats de ces sols, et d'autre part sur des extraits organiques, afin d'évaluer respectivement la toxicité liée aux polluants solubles dans l'eau et celle des polluants moins solubles ou liés aux constituants du sol.
Ce couplage lixiviation/extraction avec des biotests de toxicité aiguë, chronique et génétique permet de définir une procédure de caractérisation du danger lié aux terres contaminées. Cette procédure permet d'évaluer la mobilité et la nature des polluants responsables de la toxicité mesurée. Elle peut être utilisée pour (i) caractériser le danger lié aux terres souillées, (ii) hiérarchiser les priorités d'intervention et localiser lors de l'audit du site les zones les plus contaminées, (iii) juger de la réussite d'un traitement et (iv) suivre les mesures de protections décidées.

Contaminated Soil '98, Thomas Telford, London, 1998, 355–364

INTRODUCTION

Soils are increasingly becoming receptacles for a wide range of hazardous chemicals generated by human activities. These toxic or genotoxic compounds and their degradation metabolites may endanger human health, but also soil and aquatic ecosystems by directly affecting soil biota or, after runoff and percolation water or groundwater biota. Pollutants may change microorganisms biodiversity and activities [1-3], alter microfauna [4,5] and flora [6]. Thus, methods are needed to assess the likely impact of toxic and/or genotoxic substances.

Usually this is done by physical and chemical measurements on soil samples, but chemical analysis cannot provide a valid basis for hazard and risk assessment due to the fact that (i) chemical analysis is restricted to a limited list of defined and extractable compounds, (ii) some measurements are based on sum parameters to determine broader classes of chemical compounds (e.g. total hydrocarbons or PAHs) with a high heterogeneity of toxic properties for environmental targets, (iii) the bioavailability of organic and inorganic pollutants can vary considerably depending on the contaminants, the nature of the solid matrix, and the environmental conditions through a complex coupling between physical, chemical and biological processes.

Thus, biological testing (bioassays), which consist of exposing biological organisms to pollutants and observing the effects, is an useful tool for improving hazard and risk assessment of contaminated or remediated soil : it integrates the effects of all bioavailable contaminants including those not taken into account or detected with physical or chemical measurements.

SOIL ECOTOXICITY CHARACTERIZATION

Two ways are already available to assess soil ecotoxicity [7]. The first one consists of using soil biota like bacteria, earthworms, collembola or plants. The use of these organisms has been standardized and these bioassays are frequently performed to assess the effects of pure substances on soil biota, but have to be adapted to polluted soil materials [8-10]. These bioassays, which use the whole solid matrix, are both time and space consuming, and therefore expensive.

The other way to assess soil ecotoxicity is to perform bioassays used for water quality monitoring, on water soil leachates [11,12]. By so doing, testing becomes cheaper and a quick response can be obtained. But as the soluble part of pollutants represents only a fraction of the total bioavailable pollutants, water leachates may underestimate soil ecotoxicity. Alternative extractions have been under development for a number of years to characterise the «whole » solid sample toxicity. Instead of water, these new extraction procedures use organic solvents or buffers [13-15]. Thus, by coupling water leachates and different extractions with bioassays, «hazards due to soluble molecules» and «hazards due to less soluble or soil bound molecules» can be characterised respectively.

In this study, contaminated soil sample toxicity was assessed by exposing to a set of bioassays the liquid samples obtained after different water leaching tests and organic solvent extractions. The aim was to develop an indirect exposure procedure to assess soil ecotoxicity.

MATERIALS AND METHODS

Soil samples

Two soil materials were collected on industrial sites. The first site was polluted by metallic trace elements, PCBs, chlorinated solvents and organo-phosphorus pesticides (S III), and the other by PAHs (S IV). The soil sample analysis is presented in table 1.

		S III	S IV
Soil type		industrial	industrial
Soil texture		Loamy	Sandy
Metals	Cd	30	<5
(mg/kg)	Cr	342	134
	Pb	1200	nd
	Zn	2270	2080
PAHs	Naphthalene	nd	115
(mg/kg)	Fluorene	nd	87
	Phenanthrene	nd	200
	Chrysene	nd	125
	Benzo(a)pyrene	0.25	70
PCBs	Arochlor 1242	4.5	< d.l.
(mg/kg)	Arochlor 1254	204	< d.l.
	Arochlor 1260	13.7	< d.l.

< d.l. : below detection limits
nd : Non determined parameter

Table 1. Soil characteristics

Leaching and extraction procedures

Leaching and extraction procedures are summarised in table 2 and in figure 1. All leaching and extraction steps were carried out three times.

	Liquid/Solid ratio	Leaching or extraction solvent nature	Test solvent nature	Leaching or extraction time	Filtration step
W1	1/10	Water	Water	24 h	.45µm
W2	1/10	Water	Water	2h	n.f.
P	1/10	Phosphate buff. (pH=5)	Phosphate buff. (pH=5)	2h	n.f.
M	1/10	Methanol	Methanol	2h	n.f.
Soxhlet	5/100	DCM/HEX*	Methanol**	12h	n.f.
SFE	-	CO_2/Methanol	Methanol	2h	n.f.

SFE : Supercritical Fluid Extraction
n.f.: no filtration
* Dichloromethane/Hexane (50/50)
**after dry evaporation of DCM/HEX

Table 2. Leaching and extraction procedures

Bioassays

A set of different bioassays was used to assess both acute and chronic toxicity as well as genotoxicity. The acute toxicity tests were performed on leachates and extracts, with *Daphnia magna* (crustacean), *Thamnocephalus platyurus* (crustacean), and *Vibrio fischeri* (bacteria, Microtox®). Chronic toxicity and genotoxicity testing were performed with *Pseudokirchneriella subcapitata* (unicellular algae) and *Vibrio fischeri* M169 (bacteria, Mutatox®) respectively. Table 2 lists the test species, the protocol, the type of test, the test duration used, and the measured endpoints.

Organism	Protocol	Type of test	Test duration	Endpoint
V. fischeri	[16]	Acute	40 minutes	Luminescence inhibition
V. fischeri M169	[17]	Genotoxicity	24 hours	Light re emission
D. magna	[18]	Acute	24 hours	Immobilisation
T. platyurus	[19]	Acute	24 hours	Mortality
P. subcapitata	[20]	Chronic	72 hours	Growth inhibition

Table 2. Test battery used for toxicity assessment of soil extracts

- *Vibrio fischeri* tests were carried out according to the French standard [16] with commercially sold reagents (AZUR Environmental, Carlsbad, USA) and luminescence was recorded after 5, 15, 30 and 40 min, as metallic trace elements toxicity has been proved to increase with contact time [21].

- *Vibrio fischeri* M169 (Mutatox® test) were carried out with commercially sold reagents (AZUR Environmental, Carlsbad, USA) according to the Mutatox® Manual [17]. This mutant emits no light, and reversion from the dim to bright state indicates DNA damage. This test can be carried out on environmental liquid samples with or without preliminary metabolic activation using rat liver S9 mix [22]. Soil leachates (W2) were incubated for 24 h with the bacteria, and luminescence was measured with Microtox® M500 photometer after 16, 20 and 24 hours. Positive and negative controls were also carried on at the same time to check the stability of the bacterial reagent. The soil leachate was considered to be genotoxic if the light emission was four times the background level given by the negative controls.

- *Daphnia magna* assays were performed according to the French standard [18] whereas *Thamnocephalus platyurus* were carried out according to the toxkit standard operational procedures [19].

- *P. subcapitata* were performed according to the (experimental) AFNOR standard [20] with 6.10^5 cells/ml in 10 ml experimental flasks. As leachates were not filtrated, cell counting was done on Malassez lamina, under microscope.

The toxicity of the triplicates was assessed with the Microtox® test and if the variability between samples was less than 15%, the samples were mixed together and then, assessed with the other bioassays. When methanol or acidic (pH 5) samples were assessed, a solvent control was performed in parallel to take their toxicity into account.

Figure 1 shows the flow chart of the leachate and extraction procedures.

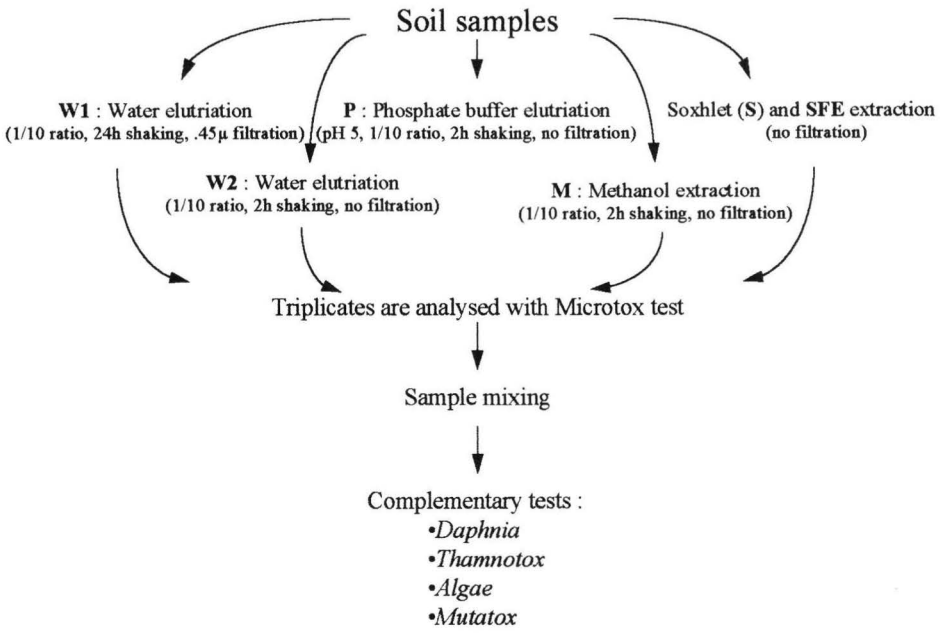

Figure 1. Flow chart of the experiments

Toxicity unit

The acute and chronic toxicity measured was expressed in toxic units (TU) according to the following formula : $TU = \frac{100}{EC_{50}\ Extr} - \frac{100}{EC_{50}\ Blank}$ where :

- EC_{50} Extr = Effective leachate or extract concentration causing a 50% decrease for the measured endpoint (in %)
- EC_{50} Blank = Effective blank (phosphate buffer or methanol) concentration causing a 50% decrease for the measured endpoint (in %)

RESULTS and DISCUSSION

• Microtox® (V. fischeri) results on soil samples S III and S IV

The results of the Microtox® tests on soil samples S III (polluted by metallic trace elements, PCBs, chlorinated solvents and organo-phosphorus pesticides) and S IV (polluted by PAHs) are given in figure 2.

No significant toxicity was observed on water leachates (W1 and W2), even without filtration (W2), or at pH = 5 (P : phosphate buffer). According to the results obtained, it can clearly be seen that potential soil hazard is mostly due to organic pollutants extracted with organic solvents.

Comparing the results for methanol (M), soxhlet (S) and SFE extractions, for soil S IV no statistical difference between these extractions was observed, whereas for soil S III, methanol extracts provide a better toxicity expression. For soil sample S III, the toxicity detected after methanol extraction was twofold that expressed on soxhlet or SFE extracts. This could be due to the nature of the soil S III pollutants which are volatile and can be lost during DCM/HEX dry evaporation and to the fact that the SFE extraction method was optimised (P, T and % co-solvent) to extract PAHs, and not PCBs or chlorinated

solvents [23]. On the other hand, for soil sample S IV, the average toxicity increases when using harder extraction methods such as soxhlet or SFE. Methanol extraction is not as successful in solubilizing pollutants such as soxhlet (stronger solvent and heating) and SFE (method developed to extract PAHs).

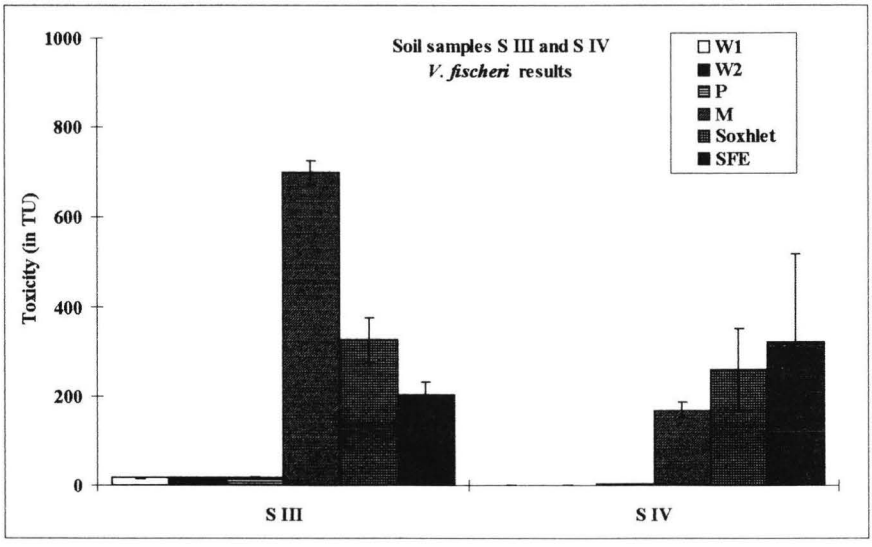

Figure 2. Microtox® (*V. fischeri*) results on soil samples S III and S IV
(W1 : Water leachate [2h, no filtration], W2 : Water leachate [24h, .45µm filtration], P : Phosphate buffer leachate, M : Methanol extract)

According to the Microtox® results, toxicity variations were less than 15% (except for soxhlet and SFE extracts on soil sample S IV) meaning that the triplicates may be mixed for complementary testing.

• *Complementary testing results on soil samples S III and S IV*

The results obtained for the other bioassays (*Daphnia, T. platyurus, P. subcapitata*) on soil samples S III and S IV are shown in figures 3 and 4, respectively. As the solvent extraction procedures were equivalent with respect to the Microtox® results, only the methanol extract results are shown.

As observed for the Microtox® results, the methanol extraction always provides an enhanced expression of toxicity on both soil samples whatever the test. Comparing the bioassays on these extracts shows that the Microtox® (on soil S III) and algae (on soil S IV) tests are more sensitive to organic pollutants than *D. magna* and *T. platyurus*. Depending on the nature of soil pollutants, bioassays sensitivity may change so that a set of different bioassays will be required to assess soil hazard.

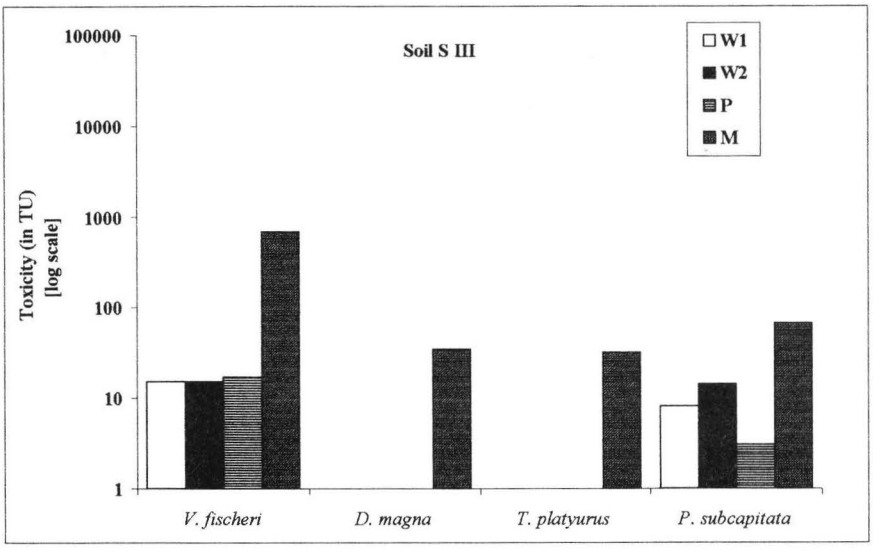

Figure 3. Bioassay results after W, P and M leachates on soil S III
(W1 : Water leachate [2h, no filtration], W2 : Water leachate [24h, .45µM filtration], P : Phosphate buffer leachate, M : Methanol extract)

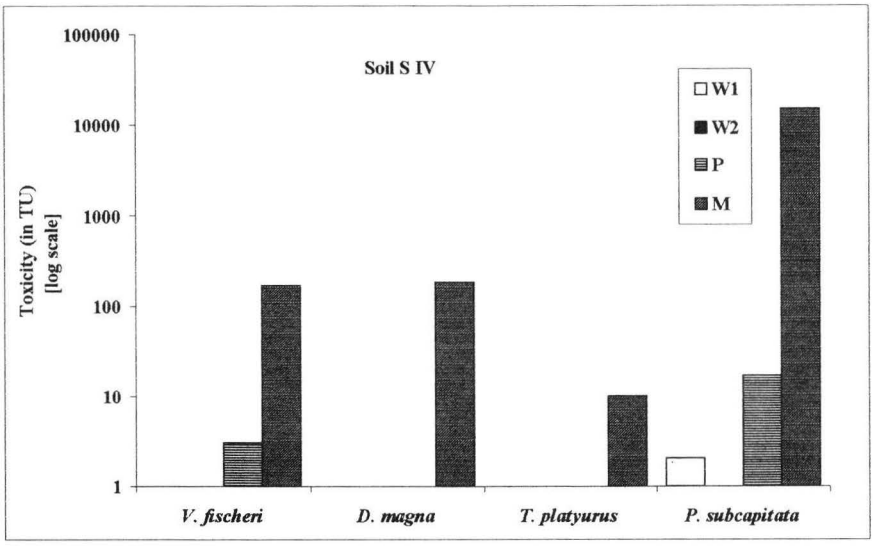

Figure 4. Bioassay results after W, P and M leachates on soil S IV
(W1 : Water leachate [2h, no filtration], W2 : Water leachate [24h, .45µM filtration], P : Phosphate buffer leachate, M : Methanol extract)

• *Mutatox® test on water leachates*

The genotoxic responses on soil samples S III and S IV, recorded with the Mutatox® test, both with and without metabolic activation, are shown in figures 5 and 6 respectively.

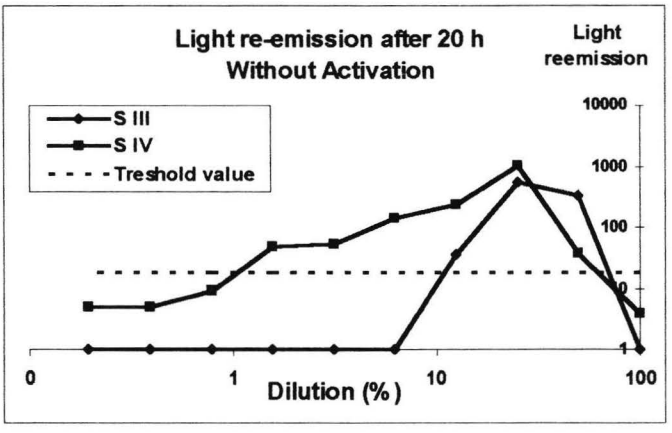

Figure 5. Mutatox® test on soil samples S III and S IV without metabolic activation, after 20 h

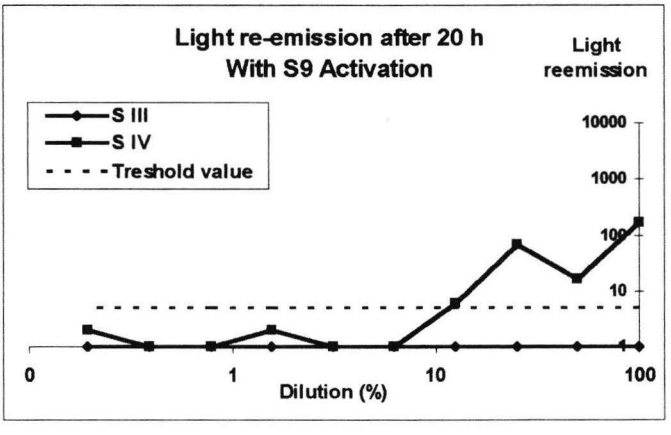

Figure 6. Mutatox® test on soil samples S III and S IV with S9 metabolic activation, after 20 h

The genotoxic responses were monitored without metabolic activation on soil samples S III and S IV, whereas after S9 metabolic activation, only soil sample S IV was still genotoxic, in keeping with the major pollutants found in this soil (PAHs). When comparing the toxicity and genotoxicity results of water leachates, it would appear that soil S IV was genotoxic but non toxic, indicating that acute or chronic toxicity information may not be enough to judge environmental hazards.

CONCLUSION

Considering the two soil samples used, the detected hazard on water leachates is only part of the potential hazard : some pollutants, due to their low solubility, may not generate high toxicity in a water leachates but are present in soil (bound to soil components) and could damage the ecosystem through other forms of exposure pathways (direct contact, ingestion of soil particles with bound pollutants) or after soil evolution. This potential hazard must also be assessed : no toxic response in the water leachate

should not be related to the abscence of hazard. According to our results, methanol extraction which is both simple (no specific equipment, no heating, no evaporation step, 2 h extraction...) and cheap, can be used to assess soil hazards due to less soluble organic pollutants. It also appears that acute or chronic toxicity may not be enough to assess the soil hazard completely and that genotoxicity must also be considered. Thus, the suggested procedure (figure 7) integrates these two aspects.

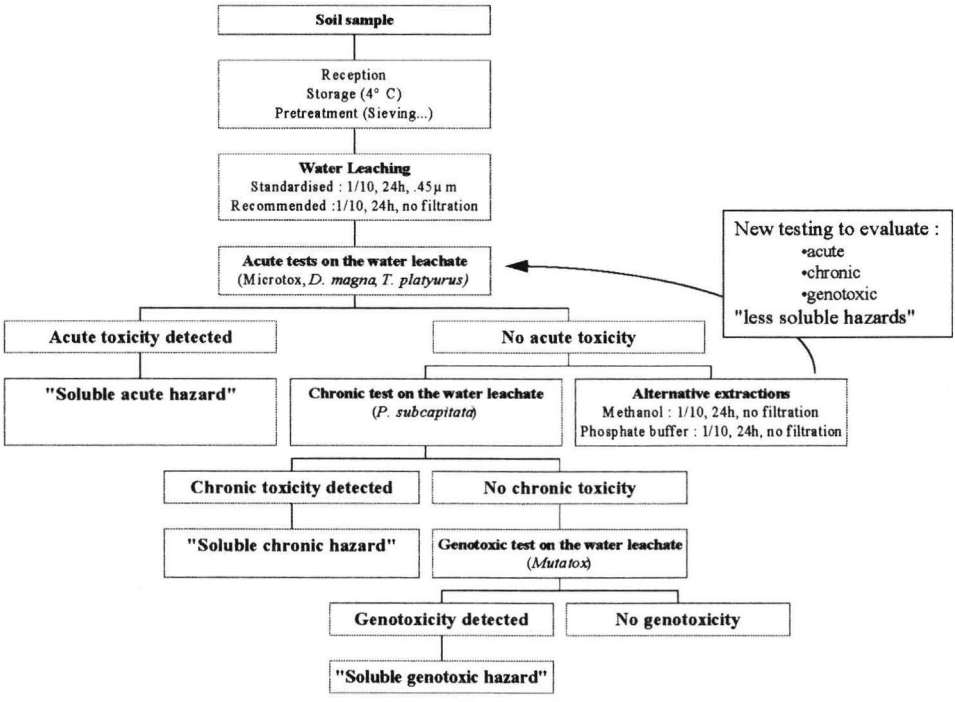

Figure 7. Procedure for soil ecotoxicity characterization

This is a step by step procedure where the chronic toxicity or genotoxicity on the water leachate are taken into account only if there is no significant acute toxicity. The same procedure should be performed with a methanol extract to reveal organic pollutant toxicity. This solvent extraction can be employed if no toxicity is detected in the water leachates or in conjunction with the latter to identify organic pollutant toxicity. The bioassay results also confirm that a test battery which integrates both different trophic levels and different kinds of effects (acute, chronic and genotoxic) is needed.

Thus, this procedure, which couples soil leachates or extracts with bioassays provides a quick and inexpensive soil sample characterization. It can be used (i) to identify hazard, (ii) to classify soil hazards and in so doing map contaminated sites qualitatively (locating more polluted areas, identifying pollutant nature ...), (iii) to monitor and judge treatment success, (iv) to control rehabilitated sites.

The authors are grateful to the French environmental agency (Ademe) and the Environmental and Climate programme of the European Commission (DG XII-DI) for their funding.

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CONTAMINATED SOIL '98

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

LIFE CYCLE ASSESSMENT FOR REMEDIAL ACTION TECHNIQUES: METHODOLOGY AND APPLICATION

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Key Words: contaminated sites, environmental impact, environmental management, environmental policy instruments, life cycle assessment, in-situ bioremediation, remedial action techniques, software tool, soil vapor extraction

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 their technical or financial aspects. The basic aspects of life cycle assessment and the specific adaptations of the method to remedial action techniques are described and the first results are illustrated with an example.

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 und erste Ergebnisse anhand eines Fallbeispieles erläutert.

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 souteraines sont expliquées. Des premiers résultats sont montrés par un exemple.

Contaminated Soil '98, Thomas Telford, London, 1998, 367–376

1 Introduction

In Baden-Württemberg, the requirements for the selection of remedial action techniques are regulated by the administrative order "Orientierungswerte". Economical and environmental aspects have to be considered in the regular weighting process. The negative potential environmental impacts produced by the remediation, so-called secondary impacts, have to be included.

Despite of the administrative order, until now it was not possible to quantify secondary impacts. 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. 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 previously established necessity of the remediation is a requirement for the application of the method presented, and a result of a multistage procedure for the assessment of contaminated sites, including a risk assessment. The method does not consider the real and potential environmental impacts induced by the cleaned-up site itself. This is done in the framework of the contaminated site assessment procedure.

Life cycle assessment is at the basis of the method, consisting of the phases goal and scope definition, inventory analysis, impact assessment and interpretation. For final decision, 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.

The method was commissioned by the town of Sinsheim, situated in the Federal State of Baden-Württemberg, Germany. It was developed by the Gesellschaft für Consulting und Analytik im Umweltbereich mbH (CAU), Dreieich under the coordination and technical management of the Technologieberatung Grundwasser und Umwelt (TGU) GmbH, Koblenz and the Landesanstalt für Umweltschutz Baden-Württemberg (LfU), Karlsruhe, financed by the public fund "Sonderabfallabgabe".

2 Methodology

2.1 Introduction

The life cycle assessment consists of a goal definition, an inventory analysis, a life cycle impact assessment and an interpretation of the life cycle assessment. Figure 1 describes the method.

2.2 Goal and scope definition of life cycle assessment

The goal and scope definition of life cycle assessment has to describe the purpose of the study, the functional unit, the system boundaries, and the data quality requirements.

The results of the life cycle assessment (secondary impacts) have the purpose to support the decision making process on the definite type and details of the remedial action technique.

All actions considered shall cut the risk to the same desired lower level and shall therefore perform the same functional unit.

The system boundaries are defined by the remedial actions, by the set of about 60 modules, by the more than 30 basic inventory tables and the set of 14 impact categories. The modules include decontamination, safe-guarding and secondary technologies. Every remedial action is a linear combination of the specific modules. The five percent limit of the cumulative energy demand has been used as cut-off criterion for ancillary inputs, according to the main contribution within one module. The tool explicitly includes the potential impacts for the local residents of the contaminated site during enforcement of the remediation measure. This goal is achieved by using subcategories for certain impact categories.

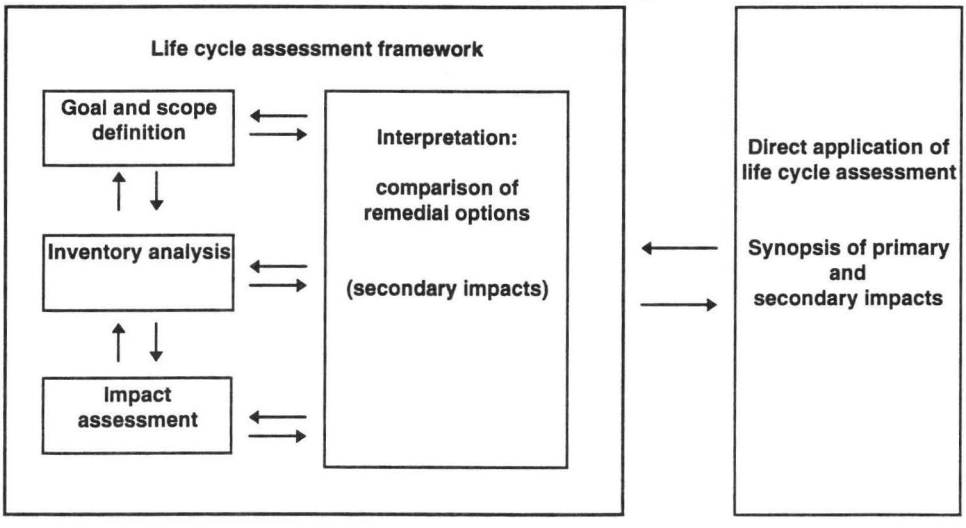

Figure 1: Remediation decision support tool based on life cycle assessment

The data quality requirement is governed by the accuracy of the input data being available at the stage of the remediation planning. The engineer estimates the amount of the polluted soil and of the mass of pollutants inside the contaminated site. He knows the suitable remediation alternatives and has general information about the details within each alternative remedial action technique. The engineer does not know the exact type, age and conditions of the used machines and the exact handling of these machines. Therefore the data base does not deal with specific machines and services but with average machines and services.

2.3 Life cycle inventory analysis

Every remediation action consumes energy and materials, which induces the consumption of other materials, all kinds of emissions and land use. In a first step the used materials and energy are documented (inputs). The remediation concept

is translated into a list of predefined modules (for example soil washing or transports). About 60 modules are fixed in this method. Most remediation technologies can be modelled with these modules.

In a second step for each module the related emissions, land use and resource consumption are calculated (outputs) linking the module data with the basic inventory tables. The Swiss "Oekoinventare für Energiesysteme" (Frischknecht et al., 1995) with many average data about energy systems (electricity, transport, ...) and some data about basic materials has been selected as the starting point for the development of basic inventory tables. The aggregated inventory table includes the data listed in table 1 and more than 100 other entries, mainly emissions.

Nr	Inventory entry	Unit
1	Cumulative energy demand KEA based on gross calorific values	Terajoule (= 10^{12} J)
2	Waste	Megagram (= 1000 kg)

Table 1: Extraction of inventory entries

2.4 Life cycle impact assessment

In a third step (impact assessment) the outputs of the inventory analysis are used to calculate potential impacts.

Type of impact category	Number	Impact category	Unit
Impact categories without differentiation between the place of the emission	3	Depletion of nonrenewable resources	Megagram/year (= 1000 kg/a)
	4	Water consumption	1000 m^3
	5	Land use	1000 m^2 a
	6	Global warming	Megagram CO_2 (= 1000 kg CO_2)
	7	Acidification	Kilogram SO_2
	8	Summer smog	Kilogram C_2H_4
	10	Human toxicity water	10^6 m^3 water
	11	Human toxicity soil	Kilogram soil
Impact categories based only on remote emissions	9	Human toxicity air (remote emissions)	10^6 m^3 air
	12	Smell (remote emissions)	10^6 m^3 air
Impact categories based only on near emissions	13	Human toxicity air (near emissions)	10^6 m^3 air
	14	Smell (near emissions)	10^6 m^3 air
	15	Noise 60 decibel (A) (near emissions)	0,1 Hours

Table 2: Impact categories

The air emissions from sources on or near the contaminated site are used to calculate the specific subcategories toxicity, smell and noise. The remote emissions are considered in corresponding subcategories toxicity and smell. Noise is not considered for remote emissions because of missing data in the aggregated basic inventory tables. All other impacts are not differentiated between a near or remote source of concerning emissions (see table 2). The characterization factors for the human toxicity, necessary for the calculation of the impact assessment have been established by the Landesanstalt für Umweltschutz Baden-Württemberg, partly published (Umwelt- und Sozialministerium Baden-Württemberg, 1993).

2.5 Interpretation of life cycle assessment

The results of the impact assessment and the inventory analysis are interpreted using all inventory entries listed in table 1 and all impact categories in table 2. According to a sensitivity analysis, impact assessment results and inventory table data (cumulative energy demand KEA, waste) are considered as significant different if the discrepancy is exceeding the factor of 2. In the interpretation a comparison between different remedial actions can be made. A dominance analysis is used to compare remediation options.

3 Example

3.1 Site and remedial action techniques under consideration

The example is based on a site that is contaminated by aliphatic and aromatic hydrocarbons from a former spill of petrol. The contaminants are located in the unsaturated zone and in the saturated zone (groundwater). The water table is about 10 m below surface level. The aquifer is build up by sandy layers with gravel. According to the site investigation there are about 400 Megagram of aliphatic and about 20 Megagram of aromatic hydrocarbons to be found in the unsaturated zone. In the saturated zone there are another 80 Megagram of aliphatic and 4 Megagram of aromatic hydrocarbons. The contaminated area is about 2000 m^2.

Owing to the spatial distribution of the contamination in the unsaturated and in the saturated zone, different remediation alternatives were taken into account in order to select the most suitable remedial action technique.

In detail the following remedial action techniques were to be considered:

Saturated zone (groundwater)

- **Long-term extraction of groundwater**

  This remediation alternative implies extraction of the contaminated groundwater by wells, used as a safeguarding measure. The groundwater is diverted into the sewerage system after the removal of the hydrocarbons by air stripping. Due to low solubility, mainly of the aliphatic hydrocarbons, the inevitable consequence of this remediation alternative is a long term extraction of groundwater.

The potential environmental impacts therefore were calculated on the basis of an estimated operation time of 50 years.

- **In-situ bioremediation in combination with a circulation system**

  This remediation alternative comprises extraction of the contaminated groundwater from wells. After the removal of the hydrocarbons by air stripping combined with adsorption to activated carbon, the water is enriched with nutrients and electron acceptors and subsequently diverted into the groundwater by infiltration wells. This circulation system helps to accelerate the in-situ bioremediation of the hydrocarbons in the saturated zone.

  The potential environmental impacts of this remedial action technique were evaluated using nitrate (NO_3^-) or hydrogen peroxide (H_2O_2) as an electron acceptor alternatively. The estimated remediation time is 5 years of operation.

Unsaturated zone

- **Soil vapor extraction**

  This remedial action technique is planned in order to clean up the unsaturated zone. The soil vapor is extracted from the subsoil by an exhaustor and subsequently cleaned-up by adsorption to activated carbon.

  Corresponding to different clean-up levels the potential environmental impacts of soil vapor extraction were evaluated on the basis of varying remediation times of 36, 29 and 22 months.

3.2 Potential environmental impacts of the remedial action techniques

The following modules were used to evaluate the remedial action techniques in the saturated zone:

- mobilisation / demobilisation of equipment
- transport of persons
- drilling and well construction (including consumption of material)
- groundwater discharge
- groundwater clean-up by air stripping
- adsorptive air clean-up by activated carbon
- mobilisation / demobilisation of activated carbon

Çoncerning soil vapor extraction the module "groundwater clean-up by air stripping" is not applicable, the module "groundwater discharge" is replaced by "air discharge".

4 Results

4.1 Remedial action techniques in the saturated zone

The result of the inventory analysis and the impact assessment is shown in figure 2. The impact categories 13 to 15 relate to the emissions directly caused on or near the contaminated site. Illustrated are long-term groundwater extraction (pump) and in-situ bioremediation, using nitrate (NO_3^-) or hydrogen peroxide (H_2O_2) as an electron acceptor alternatively.

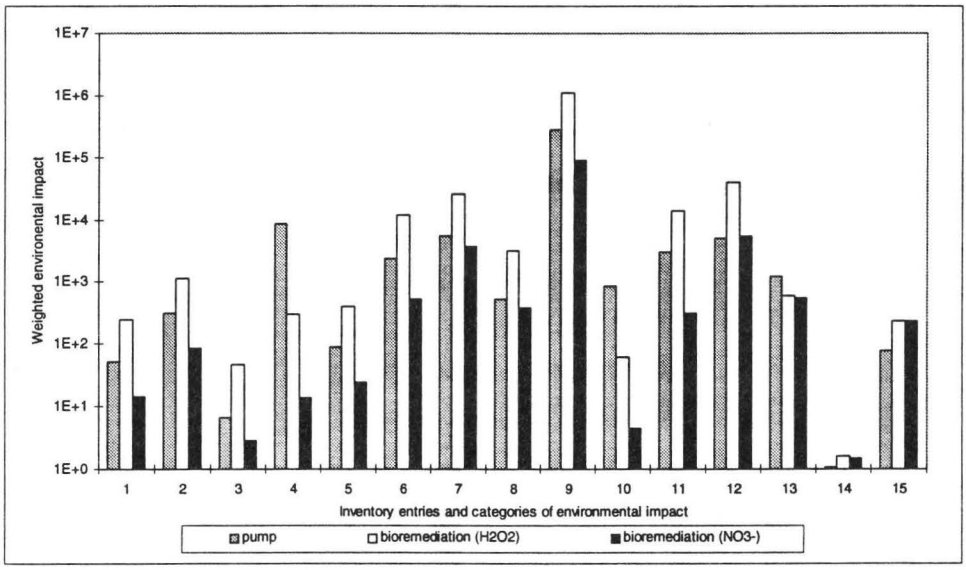

Figure 2: Result of the life cycle assessment in the saturated zone

Significant differences concerning the potential environmental impacts are evident in all categories on closer examination. For better comparison the differences illustrated above were evaluated as so-called "disadvantage factors", these factors are shown in table 3.

The disadvantage factors indicate a multiple of the least potential environmental impacts (factor 1) of each category.

The following characteristics are evident:

- In-situ bioremediation using nitrate as an electron acceptor is the least disadvantageous remedial action technique. It causes the highest potential environmental impacts only in the category noise.
- On the other side, using hydrogen peroxide as an electron acceptor, is the least suitable remedial action technique, due to the highest energy demand, the highest waste production and the biggest disadvantage factors in most of the impact categories.

disadvantage factors of the remedial action technologies in the saturated zone				
Nr.	impact category	pump	H_2O_2	NO_3^-
1	energy consumption	4	20	1
2	waste	4	10	1
3	depletion of nonrenewable resources	2	20	1
4	water consumption	600	20	1
5	land use	4	20	1
6	global warming	4	20	1
7	acidification	2	7	1
8	summer smog	1	8	1
9	human toxicity air (remote emissions)	3	10	1
10	human toxicity water	200	10	1
11	human toxicity soil	10	50	1
12	smell (remote emissions)	1	7	1
13	human toxicity air (near emissions)	2	1	6
14	smell (near emissions)	1	1	1
15	noise 60 decibel A (near emissions)	1	3	3

Table 3: Interpretation of results of the impact assessment

4.2 Soil vapor extraction in the unsaturated zone

Potential environmental impacts induced by different operating times of 36, 29 and 22 months are shown in figure 3.

The calculations substantiate the following characteristics:

- The highest potential environmental impacts are caused by an operation time of 36 months, as it was expected.
- The differences between the options of 36 and 22 months is less than time reduction of nearly 40 %; it is only 4 % to 8% for most of the inventory entries and impact categories.
- Using identical modules and basic inventory tables the minimum discrepancy for a "significant difference" is lower than a factor of two. Although the differences are quite small, they are above error level and therefore can be regarded as significant.

4.3 Conclusions

Concerning the remedial action techniques in the saturated zone, in-situ bio-remediation using nitrate as an electron acceptor was identified to be the remedial action technique with the least potential environmental impacts. Simultaneous the same technique, using hydrogen peroxide, produces the highest potential environmental impacts. The immense difference in potential environmental impacts is induced by the production of hydrogen peroxide, which is a highly energy-consuming process. This, in turn, causes depletion of resources, combined with a quantity of

emissions into air, water and soil. The potential environmental impacts of water extraction compared to an in-situ bioremediation using nitrate are also unfavourable, due to its long-term groundwater consumption.

Concerning soil vapor extraction the biggest potential environmental impacts are also correlated with the most energy consuming activities. In this case production and thermal desorption of activated carbon are by far the most energy consuming processes. Energy consumption at the same time dominates the potential environmental impacts. This is the main reason why there is no big difference in potential environmental impacts of different operation times. Energy consumption is in direct proportion to the mass of activated carbon that is needed for adsorption of contaminants. This is nearly the same for all operation times. High quantities of activated carbon are needed only in the beginning of this remedial action technique. Due to low concentrations of hydrocarbons in the last stage of a soil vapor extraction, there is no need of more amounts of activated carbon.

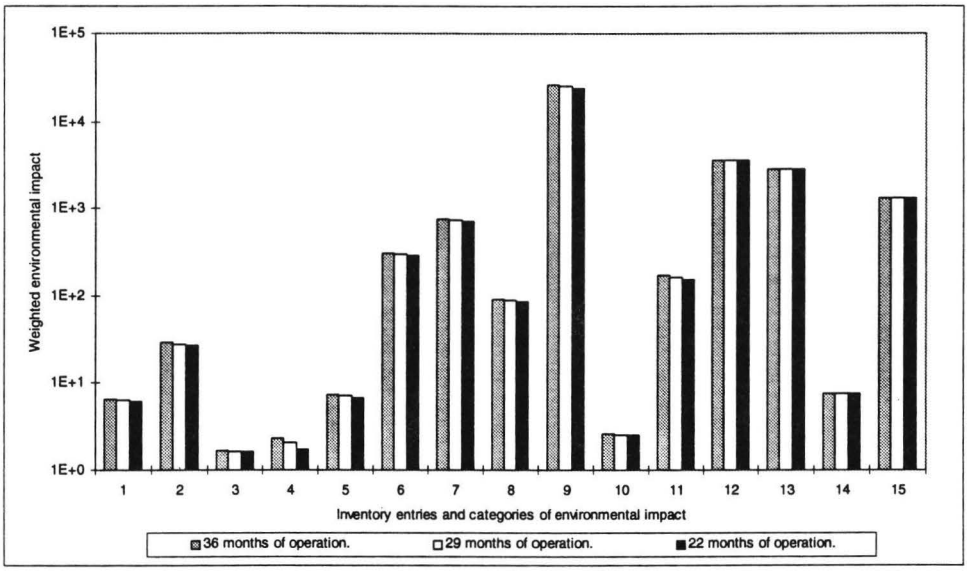

Figure 3: Result of the life cycle assessment in the unsaturated zone

5 Final remarks and further development

The method based on life cycle assessment results to a transparent decision making process, which enables the selection of remedial action techniques with least potential environmental impacts. Therefore it will be a valuable tool of decision making in order to minimize these impacts induced by the remediation or safeguarding of contaminated sites.

Additionally, it will be an environmental policy instrument for the verification of clean-up levels, especially of the suitability of various clean-up levels.

An important topic for future development is the additional integration of innovative remedial action techniques like "funnel and gate". They will be integrated as soon as the input data will be available.

The handling of the system will be faciliated by a software tool, which will be introduced to the public in October 1998 and which will be available by the Landesanstalt für Umweltschutz Baden-Württemberg at the end of the year 1998.

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DUTCH HANDBOOK ON SOIL REMEDIATION TECHNIQUES: AN EVALUATION OF PERFORMANCES OF TECHNIQUES

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Key words: in-situ methods, soil remediation, remedial action techniques, governmental directives.

SUMMARY

At the moment the Dutch Handbook of Soil Remediation Techniques is being updated. As a part of this project the performances of soil remediation techniques in 34 full-scale projects, finished or in execution, have been evaluated. It was found that due to a risk-based approach, the application of in-situ techniques is rapidly growing, especially in-situ air stripping. Remediation concepts are more and more tailor made. The majority of projects showed a combination and/or sequence of several remediation techniques. Furthermore, a comparison of the results of conventional approaches (excavation, pump and treat) and in-situ techniques clearly is in favour of the latter. The results of both are comparable, but in general in-situ techniques have more flexibility, lower environmental impact and lower cost.

KURZFASSUNG

Zur Zeit wird das Handbuch für Bodensanierungsverfahren erneuert. In einem Teil dieses Projektes wurde die Durchführung von angewandten Bodensanierungsverfahren bewertet. Insgesamt sind 34 Projekte, abgeschlossene oder laufende, betrachtet worden. Infolge von Untersuchungen, die auf einer Risikoermittlung basieren, wächst die Anwendung von in-situ-Techniken schnell, besonders in-situ-air-stripping. Bodensanierungskonzepte sind immer mehr nach Maß gemacht. Die Mehrheit der Projekte zeigte eine Kombination und/oder eine Aufeinanderfolge von mehreren Sanierungstechniken. Außerdem fällt ein Vergleich der Ergebnisse von konventionellen Verfahren (Aufkofferung, Grundwasserentnahme und -behandlung) und in-situ-Techniken deutlich zugunsten der letzteren aus. Die Ergebnisse beider Methoden sind vergleichbar, aber die Flexibilität, der geringe Eingriff auf das weitere Umfeld und die geringeren Kosten sind die Vorteile der in-situ-Techniken.

RÉSUMÉ

Le manuel néerlandais des techniques de réhabilitation des sols est en ce moment en phase d'actualisation. Les performances des techniques de réhabilitation des sols en pratique ont été évaluées comme partie de ce projet. En tout, 34 projets, terminés ou en cours, ont été examinés.
De plus en plus, le traitement des sols est jugé sur le facteur risque, c'est pourquoi l'application de ces techniques in situ s'est rapidement étendue, surtour dans des situations d'Air stripping. Les concept de réhabilitation sont de plus en plus faits sur mesure. La majorité des projets montraient une combinaison et une succession de plusieur techniques.
De plus, une comparaison des résultats d'approches conventionelles avec les techniques in situ sont clairement en faveur de ces dernières. Les résultats des deux techniques sont comparables mais, la flexibilité, l'impact environnemental peu important et les coûts peu élevés des techniques in situ les rendent plus attractives.

Contaminated Soil '98, Thomas Telford, London, 1998, 377–381

1. INTRODUCTION

The Dutch Handbook on Soil Remediation Techniques is being updated. In previous stages remediation and isolation techniques were described. Only the field of applicability of techniques could not be addressed. A sound evaluation of their performance in the field was not available. Recently a consortium of the consultants IWACO, TAUW and DHV has finished 34 audits on soil remediation projects. The project was closely guided by representatives of the authorities, research institutes (RIVM) and research programmes (e.g. NOBIS). Due to strongly diverging site specific conditions and the scarcity of finished remediation projects it was decided to perform a general evaluation of techniques in stead of a (wanted) quantitative validation.

Recently, risk-based approaches are more and more accepted by the Dutch authorities. The application and technical developments of in-situ remediation techniques both show important improvements. It is time to come to a final acceptance of in-situ techniques, an acceptance that can only be accomplished by using an objective evaluation of results of full-scale projects. Because full-scale projects not always reflect the latest developments, an integration was made between evaluation results and expert judgement of the latest state of the art.

Objectives

Main objective is to get information on the performances and field of applicability of in-situ remediation techniques, based upon an evaluation of field results. The results are transferred into Handbook texts, and must give information about performances of techniques, applicability, trends and developments.

Techniques

The evaluation was restricted to those techniques frequently applied. Not all techniques described in the Handbook were evaluated. The number of full-scale projects of some techniques is expected to be too small for a sound evaluation.

The following techniques were surveyed:

- Excavation, both below and above water level;
- Pump and treat or groundwater extraction;
- Biorestoration (wet);
- Soil vapour extraction and bioventing;
- In-situ airstripping and biosparging.

2. SITE CLASSIFICATION

Successful application of a specific soil remediation technique depends on soil properties and type and extent of contamination. In this study, several remediation projects, performed at different field sites, were evaluated. The field sites were classified by both soil type and physical appearance of the contaminant.

Soil type
The soil was divided into four types:
1) homogeneous sandy layers (50-2000 μm),
2) sandy layers containing thin layers of peat, loam or clay,
3) clay or peat layers in which some sand is included, and
4) homogeneous layers of clay or peat.

With this classification method most of the soil profiles in The Netherlands can be covered.

Physical appearance of a contaminant
The physical appearance of contaminants was divided into 6 classes:
1) Light Non-Aqueous Phase Liquid floating on the groundwater,
2) Dense Non-Aqueous Phase Liquid moving vertically through aquifers,
3) Residual Pore Volume Saturation,
4) Gaseous contaminants in the unsaturated zone that are in sorption equilibrium with the solid phase,
5) Dissolved contaminants that are in sorption equilibrium with the solid phase, and
6) Precipitations or insoluble contaminants.

Source and plume
The contaminated site is divided into two sub-areas:
1) the source of the contamination with free phase product, and
2) the plume area downstream from the source, with dissolved contaminants in equilibrium.

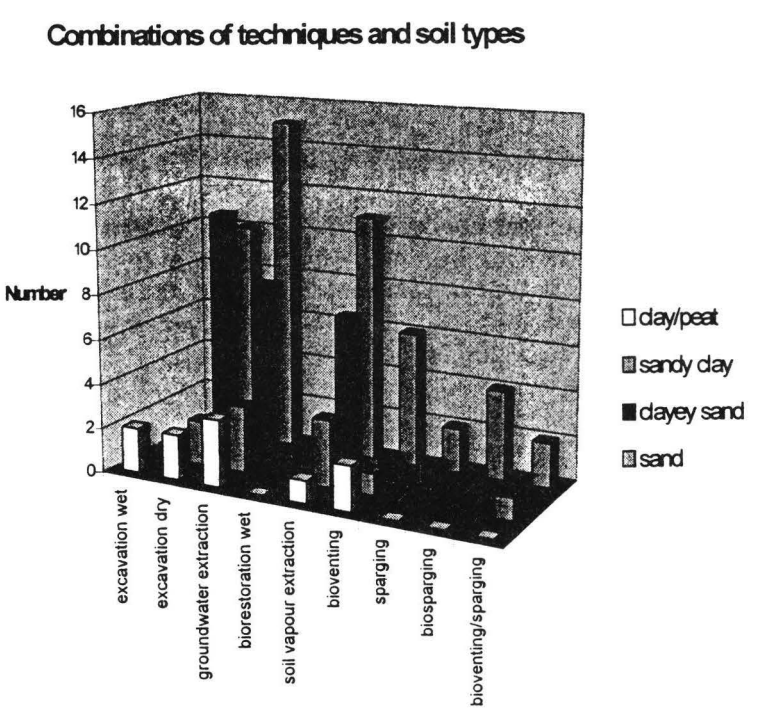
These sub-areas need a different remediation approach.

3. QUESTIONNAIRE AND AUDITS

A questionnaire was developed to acquire the information needed for this study. Questions were asked about the site (location, source, soil type, contamination type) and about the remediation techniques and their performances (decrease in concentration, time needed, cost, successes and bloopers). The questionnaire was adapted after a preliminary study. Instructions were enclosed with the questionnaire. The returned questionnaires were audited by a team of specialists.

4. SELECTION OF SITES

Thirty-four sites were selected out of a database containing about 100 sites. The selection was based upon the remediation technique that was applied, the soil type and properties of the contaminants. Again only those combinations more frequently applicated were selected. After evaluation, it was found that the site-classification method resulted in more than 80 different technique applications, combinations of techniques and soil-types (Fig. 1).



5. RESULTS AND CONCLUSIONS

General

Obviously, the number of projects evaluated is limited and recent developments could not be included. Thus the outcome of the evaluation must be regarded with some care. It was also found that a structural evaluation of remediation results is not common practice. In general some extra measurements necessary to estimate the performances of techniques were often not available.

Furthermore, technical and political developments are rapid. A frequent update of Handbooks, guidelines etc. is inevitable.

Performances of techniques

Both in-situ remediation techniques and conventional techniques (excavation/pump and treat) were applied successfully and have their specific advantages. Application of conventional techniques, however, often leads to residual soil contamination and, therefore, groundwater remediation is needed for a very long time. Although in-situ technology does not lead to complete cleansing, it is found to be more flexible, cost-effective and has

environmentally less impact.

Air- and biosparging are of increasing importance. These techniques show very good results. Unwanted side effects, as there are settling of the subsoil or uncontrolled dispersion of the contaminants, were hardly reported.

Design of in-situ systems
Soil heterogeneity is of great concern and was mentioned as the main reason for explaining disappointing results. Heterogeneity should be taken into account but is generally underestimated. A diffuse system set-up, consisting of many small elements with small distances, is recommended.

In sandy soils with loamy layers, the impacts of the loamy layers are often underestimated.

Remediation strategies and developments
In-situ remediation is developing from application of a single technique to application of concepts and strategies in which different in-situ techniques are involved. Instead of selecting one technique, remediation strategies must be developed. The distinction between source and plume, hot-spot removal and e.g. natural attenuation is needed for an effective approach.

Technological and political changes in The Netherlands (risk-based strategies) more and more make the application of in-situ techniques more favourable. It is expected that the application of innovative techniques such as bio-walls, rusty walls, natural attenuation, funnel and gate, phytoremediation, etc. will increase in the future.

After a long period of merely conventional techniques, in the Netherlands, the time is right for innovative strategies and concepts.

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ESTIMATION OF EFFECTIVENESS OF TREATMENT TECHNOLOGIES FOR CONTAMINATED SOIL AND GROUNDWATER

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Key words: sampling program, monitoring procedures, quality assurance, quality control, quality standards, clean-up technologies, remediation efficiency.

SUMMARY

Under a bilateral agreement between the U.S. Environmental Protection Agency (EPA) and the German Federal Ministry of Education, Science, Research and Technology (BMBF), ten innovative technology demonstrations were conducted in the U.S. and Germany between 1991 and 1996 to evaluate the effectiveness of the treatment technologies on contaminated soil and groundwater. All demonstrations were subject to EPA quality assurance requirements and German requirements. This paper outlines the primary results of the demonstration and highlights selected differences in the EPA and German approaches to ensuring quality in estimating the effectiveness of treatment technologies.

KURZFASSUNG

Im Rahmen einer Zusammenarbeit zwischen dem Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie (BMBF) und der United States Environmental Protection Agency (EPA) wurden zwischen 1991 und 1996 in der Bundesrepublik Deutschland und den USA insgesamt 10 Technik-Demonstrationen zur Feststellung der Leistungsfähigkeit von Altlastensanierungsanlagen durchgeführt.

Die Demonstrationen erfolgten nach den Vorgaben des Qualitätsmanagements der EPA und entsprechender Untersuchungsmethoden auf deutscher Seite. Im vorliegenden Beitrag werden die Ergebnisse der Technik-Demonstrationen in Deutschland und in den USA im Überblick zusammengefaßt und die Unterschiede im Qualitätsmanagement bei der Bewertung von Dekontaminationstechniken herausgestellt.

RÉSUMÉ

Aux termes d'un accord bilatéral entre l'Agence de Protection de l'Environnement des États-Unis (EPA) et le Ministère Fédéral Allemand de l'éducation, de la Science, et de la Technologie (BMBF), dix démonstrations innovatrices de technologie ont été conduites pour évaluer l'efficacité des technologies de traitement sur le sol et les eaux souterraines souillés. Chacun des dix a été soumis aux conditions de garantie de la qualité d'EPA et aux conditions allemandes. Cet article trace les grandes lignes des résultats primaires de la démonstration et met en valeur des différences choisies dans l'EPA et l'Allemand s'approche à assurer la qualité en estimant l'efficacité des technologies de traitement.

Contaminated Soil '98, Thomas Telford, London, 1998, 383–392

INTRODUCTION

The United States Environmental Protection Agency (EPA) and the German Federal Ministry of Education, Science, Research and Technology (BMBF) entered into a Bilateral Agreement in 1990 to gain a better understanding of each country's efforts in developing and demonstrating remedial technologies. The goals of the bilateral agreement are to (1) facilitate an understanding of each country's approach to the remediation of contaminated sites, (2) demonstrate innovative remedial technologies as if the demonstrations had taken place in their native country, and (3) facilitate international technology exchange.

Ten technologies at sites in the U.S. and in Germany have been tested and evaluated under the first phase of the Bilateral Agreement. Technology evaluations occurring in the U.S. correspond to EPA Superfund Innovative Technology Evaluation (SITE) demonstrations; those occurring in Germany correspond to full-scale site remediation activities. In the case of the U.S. evaluations, demonstration plans are prepared following routine SITE procedures. Additional monitoring and evaluation measurements required for evaluation of the technology under German regulations were specified by the German partners. For the demonstrations occurring in Germany, the German partners provided all required information to allow the U.S. partners to develop an EPA Category II Quality Assurance Project Plan.

EPA QUALITY MANAGEMENT

EPA's National Risk Management Research Laboratory (NRMRL) approaches quality management of the SITE Program from two perspectives: program quality management and project quality management. Both the SITE Program and individual technology evaluation projects are comprised of quality management activities in the areas of planning, implementation, assessment and response, and reporting.

SITE Program planning is performed by NRMRL management, the SITE Program Manager, EPA SITE Program personnel, NRMRL quality assurance (QA) personnel, and SITE Program customers (e.g., Congress, EPA Regional Offices, states and federal agencies, etc.). The SITE Program Manager is responsible for developing a "strategic plan" to indicate how the SITE Program will operate. NRMRL SITE Program personnel are currently developing a Quality Management Plan to formalize the SITE Program's policies and procedures. These policies and procedures document how the SITE Program is implemented and the responsibilities of EPA SITE Program personnel. The SITE Program also plans how it will select technologies for demonstration and contractors to assist in the implementation of SITE projects. Standard technical selection criteria are used to provide a consistent selection process.

SITE Program implementation is currently assessed through yearly program reviews by the NRMRL Director; periodic management system reviews; and periodic reviews by the Government Accounting Office and Inspector General. These reviews identify areas where the SITE Program can be improved. The SITE Program Manager is responsible for responding to these assessments by documenting corrective action that has addressed or will address the issues identified by the reviewers. The SITE Program also performs bi-annual reviews of contractor performance to assess contractor support. The SITE Program documents its progress in annual reports to Congress.

At the project level, planning is coordinated by a Project Manager. All project participants (the technology vendor, the laboratories responsible for data analysis, other state and federal agencies, QA personnel, etc.) participate in planning the technology demonstration. The planning document describes: the technology to be demonstrated; project objectives; project organization; experimental design; sampling and analytical procedures; QA objectives and quality control; and data reduction, validation and reporting procedures. The planning document is reviewed by a NRMRL QA professional to assess compliance with SITE Program requirements. The NRMRL QA professional documents nonconformances (findings and observations) to the Project Manager who is responsible for resolving nonconformances. All findings must be resolved prior to data gathering, data generation, or measurement activities.

Data producers are responsible for implementing the planning document as written. If procedures change, the Project Manager is responsible for ensuring that changes are documented. If changes are significant, a NRMRL QA professional must review the changes. The Project Manager oversees project implementation.

During the early stages of implementation, a NRMRL QA professional performs on-site assessments of project activities (sampling and analytical) to ensure that the planning document is being implemented as written. The NRMRL QA professional documents any areas of nonconformance to the planning document that could significantly impact data quality or the attainment of a project objective. The Project Manager is responsible for responding to the assessment by documenting corrective action to address each nonconformance. The Project Manager is also responsible for ensuring that corrective action is implemented.

Upon completion of the project, the SITE Program in collaboration with the data producers documents the results of the project in an Innovative Technology Evaluation Report (ITER). The ITER summarizes all data generated, including quality control data, and presents project conclusions. The ITER is supported by a Technology Evaluation Report (TER) which includes the final EPA-approved planning document, and more fully documents the raw data. The ITER and TER are reviewed by a NRMRL QA professional to ensure the conclusions are supported by credible data. Once the NRMRL QA professional documents acceptability of the reports, the Project Manager places the TER in the project file and the ITER is published and distributed to interested parties.

QUALITY MANAGEMENT IN GERMANY

Compared to the centralized approach of the EPA to quality management, the German approach reflects different responsibilities and traditions.

The responsibility for regulations and permitting procedures with respect to remediation is located at the State and not at the federal level. Therefore, a broad range of regulations and official publications concerning planning, management, evaluation, and documentation are published, but are only valid in the specific state.

The organization and responsibilities for projects in Germany can be divided into 4 main groups:

- Authorities

  The responsible authority can initiate activities such as site investigations, monitoring, permitting, responsible party identification, and remediation. The organization

and responsibilities within the authorities is typically provided in organizational handbooks. Theoretically, the fundamentals for a quality management plan are given. Even if the practical work is delegated to a contractor, the responsibility for quality management belongs to the authority (DIN ISO 9001). However, a quality management system is not mandatory.

- Site owner / responsible party

  The contamination can be cleaned-up by the owner / responsible party of a site. The owner / responsible party is responsible even if a consultant is hired to manage the investigation or the remediation.

- Consultant/Engineers

  Consultants are responsible for their work within a specific contract. It is expected that their service is of "good quality", and it is not generally required for these groups to have a certified quality management system. A European Union regulation (92/50/EWG, dated 18. July 1992) that addresses quality requirements for consultants working under public contracts is yet not implemented in German regulations.

- Laboratory

  The laboratory is responsible for the analysis of the samples. Usually the laboratory is not asked to analyze QA/QC samples and no parameters describing the data quality are documented in a report to the site owner or consultant. Often, the history of the incoming samples is poorly known in the laboratory and the laboratory personnel are not involved in the decision-making process concerning sampling and sampling strategy.

  Laboratories involved in remediation usually have an accreditation based on DIN EN 45001; this includes a quality management system and required documentation and reporting. Since the German market has shown decreased prices for analytical work in recent years, maintaining such a system may be financially difficult for the laboratory.

The Federal Soil Protection Act (Bundesbodenschutzgesetz BBodSchG) is still not enacted. It is expected that the Soil Protection Act will require a minimum of quality management standards (e. g. planning of remedial action, sampling & analysis, statistical evaluations, cleanup limits) which allows further regulations by the specific states.

A roundtable "Quality Assurance Group" (Arbeitsgruppe Qualitätssicherung des LAGA-Altlastenausschusses) of the responsible state ministries is currently developing standards for planning of site investigations (sampling strategy, sampling, analysis, and documentation). Additionally, on the federal level, an approach to investigation and remediation on some federally-owned or -managed sites has been developed by the Oberfinanzdirektion (Main Financial Agency) Hannover and funded by the Federal Ministry for Planning, Building and Urban Development (Bundesbauministerium) which is responsible for these sites. This approach included criteria for the accreditation of laboratories.

QA requirements are not yet standardized and are primarily implemented at the discretion of the project manager and the laboratory (Scola et al., 1995). A systematic approach to quality management which defines the central responsibilities of the site owner, the authority, or the project management is still missing in most of the projects.

OBJECTIVES OF SITE TECHNOLOGY DEMONSTRATIONS

The EPA SITE Program is a formal program to accelerate development, demonstration, and use of new or innovative technologies for site cleanups. The program has four goals:

- Identify and, where possible, remove impediments to development and commercial use of alternative technologies
- Conduct a demonstration program of the more promising innovative technologies to establish reliable performance and cost information for site characterization and cleanup decision-making
- Develop procedures and policies that encourage selection of available alternative treatment remedies at uncontrolled hazardous waste sites
- Structure a development program that nurtures emerging technologies

The SITE demonstration program is administered by EPA's Office of Research and Development (ORD) at NRMRL in Cincinnati, Ohio.

SITE program demonstrations are usually conducted at uncontrolled hazardous waste sites such as EPA removal and remedial action sites, sites under the regulatory jurisdiction of other federal agencies, state sites, EPA testing and evaluation facilities, sites undergoing private cleanup, the technology developer's site, or privately owned facilities.

Technology demonstrations under the SITE program focus on the pilot- or field-scale stage of operation. The technologies EPA selects for demonstration under the SITE program have already been tested at the laboratory- or bench-scale level. The main objective of the SITE demonstration program is to develop reliable performance and cost data on innovative, alternative technologies. The emphasis of the SITE program is to collect performance data of known quality. Therefore, the procedures used in conducting sampling and analysis are critical, and approved quality assurance and quality control (QA/QC) procedures must be stringently applied throughout the demonstration.

The demonstration and evaluation process yields the following information about the technology by assessing sampling and analytical results, and other available and verifiable information:

- Effectiveness of the technology in treating target contaminants
- Potential need for pre- and post-treatment processing of raw and treated materials
- Site-specific wastes and media to which the technology can be applied
- Potential site-specific system operating problems and their possible solutions
- Approximate capital, operating, and maintenance costs
- Projected long-term operating and maintenance costs

RESULTS OF THE TECHNOLOGY DEMONSTRATIONS IN THE U.S. AND GERMANY

Tables 1 to 10 provide an overview of the results of the specific technology demonstrations conducted under the first phase of the Bilateral Agreement. The tables focus on

the primary objectives and other major aspects of the demonstrations. These results are based on the data which were collected during the demonstrations in the U.S. and Germany.

Detailed results are published by the German Federal Environmental Agency UBA in 3 reports (Steffens, et. al. 1998) and by the EPA as Innovative Technology Evaluation Reports. An example of a test plan and QA objectives are also given by Steffens et al. (1995).

Table 1: Summary of the results of the NORDAC soil washing demonstration within the Bilateral Agreement U.S. EPA - BMBF Phase 1

NORDAC Soil Washing, Hamburg	
medium: soil	contaminant: VOC, BTEX
removal efficiency (BTEX)	97,5 %
removal efficiency (PAH)	99,7 %
removal efficiency (TRPH)	98,8 %
concentration (VOC/BTEX untreated soil)	average: 1.850 mg/kg
concentration (VOC/BTEX treated soil)	49,1 mg/kg (95% confidence level)
comments/remarks: • major differences between routinely performed analysis and data of the demonstration	

Table 2: Summary of the results of the Harbauer vacuum distillation demonstration within the Bilateral Agreement U.S. EPA - BMBF Phase 1

Harbauer Vacuum Distillation, Marktredwitz	
medium: soil	contaminant: Hg
removal efficiency (Hg)	97,4 %
removal efficiency (Hg, TCLP)	93 %
process water (Hg)	5 µg/l
emissions (Hg)	1,9 to 4,6 µg/m³
concentration (Hg, untreated soil)	average: 875 mg/kg
concentration (Hg, treated soil)	average: 21,36 mg/kg 24,06 mg/kg (95% confidence level)
comments/remarks: • treatment criteria / limit of the project was 50 mg/kg • minor differences between routinely performed Hg check and data of the demonstration	

Table 3: Summary of the results of the Hochtief thermal desorption demonstration within the Bilateral Agreement U.S. EPA - BMBF Phase 1

Hochtief Thermal Desorption, Herne	
medium: soil	contaminant: BTEX, PAH, TRPH
removal efficiency (BTEX)	97,89 %
removal efficiency (BTX)	99,14 %
removal efficiency (PAH)	99,65 %
removal efficiency (TRPH)	98,78 %
average concentration (untreated soil)	BTEX: 130 mg/kg PAH: 8314 mg/kg TRPH: 1518 mg/kg
concentration (treated soil at 95% confidence level)	BTEX: 1,43 mg/kg PAH: 0,0 to 8,5 mg/kg TRPH: 16,91 mg/kg

Table 4: Summary of the results of the Umweltschutz-Nord, microbiological reactor and pile demonstration within the Bilateral Agreement U.S. EPA - BMBF Phase 1

Umweltschutz-Nord TERRANOX, Ganderkesee	
medium: soil	contaminant: CHC, TRPH
removal efficiency (VOC, reactor + pile)	94,9 %
removal efficiency (VOC, reactor)	67,3 %
removal efficiency (TRPH)	31,0 %
comments/remarks: • major differences between data based on DIN method (MKW) and EPA method (TRPH)	

Table 5: Summary of the results of the RUT TERRA-POR thermal desorption demonstration within the Bilateral Agreement U.S. EPA - BMBF Phase 1

RUT TERRA-POR low temperature thermal desorption, Bottrop	
medium: soil	contaminant: PAH
removal efficiency (PAH)	79,91 %
concentration (PAH, untreated soil)	average: 2450 mg/kg
concentration (treated soil at 95% confidence level)	PAH: 11,6 mg/kg
comments/remarks: • thermally treated soil should be carefully analyzed by different methods	

Table 6: Summary of the results of the Entsorgungsbetriebe Duisburg / ZÜBLIN KNV demonstration within the Bilateral Agreement U.S. EPA - BMBF Phase 1

Entsorgungsbetriebe Duisburg / ZÜBLIN catalytic oxidation (KNV), Duisburg	
medium: soil air, stripp air	contaminant: VOC/BTEX
removal efficiency (VOC/BTEX)	98,53 %
concentration (VOC/BTEX, treated air)	< 5 mg/m^3 (95% upper confidence level)

Table 7: Summary of the results of the SoilTech ATP demonstration within the Bilateral Agreement U.S. EPA - BMBF Phase 1

Soil Tech Anaerobic Thermal Processor, Waukegan	
medium: soil / sediment	contaminant: PCB / dioxins/furans
removal efficiency (PCB)	99,97 to 99,99 %
destruction and removal efficiency DRE	PCB: 99,9999902 % dioxins/furans: 99,9999025 %
concentration (untreated soil)	PCB: 8.673 to 12.241 mg/kg TCDD (EPA): 95µg/kg
concentration (treated soil)	PCB: 1,45 to 2,65 mg/kg TCDD (EPA): 0 µg/kg

Table 8: Summary of the results of the SVVS® demonstration within the Bilateral Agreement U.S. EPA - BMBF Phase 1

SVVS® Subsurface Volatilization and Ventilation System, Buchanan	
medium: soil	contaminant: VOC
removal efficiency (VOC)	VOC: 80,6 %
concentration (VOC, untreated soil)	341,5 mg/kg
concentration (VOC, treated soil)	66,2 mg/kg
comments/remarks: • data obtained by DIN 38407 F5 and SW 8468010/8020 are similar for VOC > 1.000 µg/kg	

Table 9: Summary of the results of the perox-pure™ demonstration within the Bilateral Agreement U.S. EPA - BMBF Phase 1

perox-pure™ Chemical Oxidation Technology, Tracy	
medium: groundwater	contaminant: VOC
removal efficiency	TCE: 99,7 % PCE: 97,1 % chloroform: 93,1 % DCA: 98,3 % TCA: 81,8 % AOX: 98,5 %
drinking water action levels	O.K. (95 % confidence level)
concentration (treated water)	TCE, PCE, DCA: < 5 µg/l chloroform: 15 µg/l TCA: 30 µg/l
comments/remarks: • the H_2O_2 concentration in the output should be < 10 mg/l for toxicological reasons	

Table 10: Summary of the results of the IITRI RFH demonstration within the Bilateral Agreement U.S. EPA - BMBF Phase 1

IITRI Radio Frequency Heating RFH, San Antonio	
medium: soil	contaminant: SVOC, VOC, TRPH
removal efficiency • heating zone • treatment zone	TRPH: 95 % 60 %
comments/remarks: • the removal efficiency and the concentrations in the heating and treatment zones and outside these zones are showing insufficient results due to migration processes and byproducts • the demonstrated treatment system was still in the process of development	

CONCLUSIONS OF THE RESULTS

The results of the demonstrations performed as part of the Bilateral Agreement between BMBF and U.S. EPA clearly show major differences in the approach to quality management. The focal points are:

- For SITE demonstrations, EPA is responsibility for QA and contracting; there is no such central responsibility in Germany
- EPA-approved methods versus "Experts-to-the-front approach" used in Germany
- U.S. approach to QA planning includes establishment of numerical QA objectives
- U.S. approach requires independent QA oversight
- Greater number of project and laboratory QC samples for SITE demonstrations than for typical German projects
- Detailed documentation and validation of results against project objectives and QA objectives in the U.S.

The analytical methods (for example, SW 846, MCAWW, and DIN) are often similar and can be performed in laboratories in the USA and Germany. If major differences are identified, a documentation of the method and a complete documentation of QA results

will increase acceptance on both sides. The transfer of technology and experience will profit from the experience of the Bilateral Agreement between BMBF and EPA.

FURTHER PROCEEDINGS OF THE BILATERAL AGREEMENT

Based on the results of Phase I of the Bilateral Agreement and the experience with the commonly used approach to quality management in Germany, the BMBF funded a second phase of the Bilateral Agreement with the major objective of developing and evaluating a German standard procedure for technology evaluation called DETAD (Deutscher Technikstandard Altlasten Dekontamination). The DETAD should:

- adapt suitable elements of the SITE approach
- take the German experience and situation into account
- include input of representatives and permitting agencies of the Bundesländer (states)
- be tested under joint BMBF - U.S. EPA technology demonstrations

In addition to developing the DETAD, the second phase of the Bilateral Agreement will focus on standards for monitoring hazardous waste sides (DEMAS; Deutscher-Monitoringstandard-Altlasten-Sicherung). Siebert et al. (1998) are giving an overview of Phase II of the Bilateral Agreement at ConSoil'98.

For the EPA, the Bilateral Agreement along with the necessity of the SITE Program to operate in a Global Environment has accentuated the need to formalize SITE Program policies and procedures according to the international standards (ANSI/ASQC-E4). This effort will provide more consistency in implementation and increase accountability among SITE Program participants.

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Band 2: In Deutschland durchgeführte Technikdemonstrationen
Band 3: In den USA durchgeführte Technikdemonstrationen

The German part of the Bilateral Agreement is funded as an R&D project by the German Federal Ministry of Education, Science, Research and Technology (BMBF) under Contract-No. 1471101.

THE REMEDIATION OF THE WARFARE-RELATED CONTAMINATED SITE STADTALLENDORF – STATE OF AFFAIRS AND EXPERIENCE

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Key-Words: groundwater-protection, public awareness, remedial action concept,

SUMMARY
The remediation of contaminated sites has become a complex process that needs an effective project management. The fact that people live on contaminated sites extends the complex situation by a further determining problem field. Instruments and structures must be provided which allow public participation. Instruments and experiences made at the Stadtallendorf site are reported.
The state of affairs of the remediation process is described and the experiences of the first remediation aerea are discussed.

KURZFASSUNG
Die Sanierung von Altlasten ist ein komplexer Prozess, der ein effektives Projektmanagement erfodert. Die Tatsache, daß Menschen auf den Altlasten leben, fügen ein weiters bestimmendes Problemfeld hinzu. Instrumente und Strukturen, die eine Beteiligung von Betroffenen ermöglichen, müssen entwickelt werden. Es wird über Erfahrungen berichtet, die im Projekt Stadtallendorf gemacht wurden. Darüberhinaus wird der Sachstand im technischen Sanierungsprozeß für den Rüstungsaltstandort berichtet und Erfahrungen aus einem ersten Sanierungsareal werden diskutiert.

Contaminated Soil '98, Thomas Telford, London, 1998, 393–402

1 PREFACE

The remediation of contaminated sites has become a more and more complex area of responsibilities. On the one hand, this results from the scope as regards content and the problems of interdisciplinarity connected with that and the great number of coinciding interests, on the other hand, from the necessity to deal with uncertainties and risks resulting from deficits in knowledge, missing obligatory conventions, contaminated site specific incalculabilities and the often experimental character of procedure and measures.

As a consequence there is the necessity of a cooperation between contractors of different special domains, of authorities responsible for different facts, of local administrations and other supporters of public interests. This can, however, only be guaranteed by structured and objective-oriented activities within the framework of an effective project management.

At the Hessian warfare-related contaminated sites these tasks are, on the one hand, in the responsibility of the Land Hesse, represented by the regional authorities as contract awarder and the HIM-ASG as the remediation contractor for the commercial remediation of contaminated sites. The strategically oriented project management (PM) that develops and defines objectives as regards content and related to costs and time and that controls the observance or directs their adaptation and further development is task of the regional councils. For the execution they use the HIM-ASG. Apart from that the HIM-ASG as the project controller is concentrated on operative controlling (content/quality, time and costs) of measures.

The division remediation of contaminated sites of the Hessische Industriemüll GmbH (HIM-ASG) was given the project management for the investigationl, remediation of the contaminated site Stadtallendorf effective as of January 1, 1993.

Since 1989 the HIM on behalf of the Land Hesse is responsible for the remediation of contaminated sites in such cases, where responsible parties for the remediation can not at all or not in time be made paying the costs for the remediation. For that the HIM in 1990 established an own division remediation of contaminated sites (ASG).

In 1997 the ASG in Hesse managed 66 projects with a financial volume of approx. 60 mio. DM. Apart from state funds also funds of the BMBF from the supporting program "model remediation of contaminated sites" are available for the remeditation in Stadtallendorf.

2 PROJECT MANAGEMENT AND PARTICIPATION OF CITIZENS

The fact that people live on contaminated sites extends the complex situation by a further determining problem field. For the people affected the announcement, all the more carrying out the remediation of contamineated sites, means a severe intrusion, which arouses consternation as regards health, psychogical, physiological as well as economical and legal consternation. The remediation of inhabited contaminated sites considerably differs from other remediation projects. With that a technical-economic-ecological problem gets a social component.

For the people affected the reason for a remediation of warfare-related contaminaed sites is often only indirectly comprehensible. Different as for example at urban development remediation, where the necessity is understandable and apart from that positive changes are foreseeable or become visible. Remediation of contaminated sites is an intrusion, which after being finished should be invisible. Therefore it becomes necessary to develop a positive future-vision, to describe or develop advantages

resulting in connection with the remediation in a goal-directed way, eg. a combination with surface recycling, structural development or enhancing the status of urban development and improvement of the infrastructure.

Project management in the remediation of contaminated sites is based on experiences in other ranges of application. In the following points of view are described, which result from the fact that the locations are inhabited.

2.1 Project preparation

In the phase of project preparation and planning the PM develops the essential structures for the organization and implementation of the project.
This includes:

- Investigating information on the location (history, development, social structure)
- Determining the circle of people affected (also include the direct surroundings)
- Determining existing (formal/informal) structures (societies, parties, churches, schools, etc.)
- Structured questioning for goals
- Working out goal conflicts (eg. industrial development/utilization of groundwater)

At planning the project organization structures must be provided, which allow a participation of people affected (or their representatives) in the preparation of decisions in the remediation process. (Public participation). Apart from the decision structures transparent, understandable decision criteria (why are the decisions taken in the way they are?) must be developed and documented.

In structures and procedures the possibilities of persons normally working on a honorary basis (length, frequency and time of the meetings) and the access to specialized knowledge must be taken into consideration. In case of hindrances or deficits it should be thought about expense allowances or a financed technical consultant at the choice of the poeple affected.

For this public participation the HIM-ASG pursues the following goals:

- consideration of all interests affected
- supporting people affected at the articulation of interests
- transparency of decisions
- accessibility of all project-related information
- reaching a consensus, dialogue-oriented way of procedure, cooperation

For the discussion of facts with fundamental importance for the total site (eg. remediation conception, remediation agreement, priorities) representative instruments of the people affected are useful. Condition is the majority acceptance of the form of the body chosen (project advisory council) and of the acting participants by the people affected. The composition depends on the project-specific situation. An extensive access to the project information must be provided. The competences (decisions, recommendations) and the catalogue of subjects of discussion must be agreed. Project advisory councils have been provided in the Hessian contaminated site law since 1994.

In the project Stadtallendorf an essential function in this connection is fulfilled by the PublicParticipationOffice (PPO), which is sponsored by the HIM-ASG and the municipality Stadtallendorf, which is financed by the Land Hesse and the tasks of which are the conveyance of information (from and to the people affected) and the support of the people affected at the articulation of their interests. Apart from that it plays an important part at drafting the remediation agreements. The

PPO operates independently of directives given by the municipality and the HIM-ASG. It has access to all information and meetings and supports the HIM-ASG at the operative project controlling (in particular in connection with the remediation).

The discussion of problems related to partial remediation areas or estates takes place in information events for small groups or in individual conversations. The continuity of contact partners is of advantage.

Planning processes (for investigation and remediation measures) have been organized in such a way that a participation of people affected and the consideration of their interests is also possible in practice. This requires extensive information and the indication of different variants. The comments of people affected are noted, examined for their feasibility, as far as that is given, taken into consideration. A rejection is explained by giving the reasons for it in writing.

Communication takes place on different levels between the project participants. For agreements between the project participants there are the following bodies:

- in a small working group the HIM-ASG, the regional council Gießen, the municipality Stadtallendorf and the PublicParticipationOffice work together, in order to agree and coordinate planned measures.
- Related to working fields or partial projects initial and status discussions are held, in which goals and procedures are determined, examined and, if necessary, are adapted. HIM-ASG, the regional council Gießen and according to demand also further persons or institutions participate in that.
- A working group of the public authority has got the task, to take votes on official decisions in connection with the remediation.

The following descriptions in particular refer to the communication with real estate owners affected, users, inhabitants, the interested public and multiplicators.

Information is given actively, in time, extensively, continuously and target group-oriented. Building up of confidence, the competence at the people affected and the acceptance of the activities planned are the goals.

Communication structures have been developed, which guarantee the conveyance of information, include forums for the exchange and the discussion of information and opinions (project advisory council, info-meetings on specific subjects and public consultation hours) and provide contact partners in the different areas/for different purposes. (PPO, site management and project management). Here project-specific conditions were taken into consideration and existing structures were used.

Instruments have been developed, which allow people affected in the different project phases the access to information (archives, PPO, estates documentation, puplic information):

- public letter to multiplicators
- development of instruments for public relations work
- public information
- brochures
- press communiqués/background information
- information meetings
- open day

Experiences made up to now show that building stable structures and a confidence basis, preferably in the (relatively simple) preparation and analyzing phase, is of importance. The different tasks and responsibilities of the participants must be fixed.

2.2 *Project realization*

Preparation and realization of the project differ considerably; the transmission takes place from the level total site to the individual property, from the theoretical arguments to the those in practice, concrete problems, which must be solved on the properties and with that also changing participants.

In the phase of project realization, the tasks of the PM include, apart from working fields eg. contract and allocation management, documentation, etc., also project controlling as regards to strategy and contents: analyzing changes in boundary conditions (finances, different state of knowledge, technical specifications) for their importance for project goals and project procedure.

The people affected must be regularly informed on the subject and the result of these reflections, structures must be provided that guarantee a participation in the preparation of decisions and the assignment of priorities. Here the project advisory council is offered to fulfill this task.

Project controlling related to operativeness and measures first has tasks known from the building and construction industry as securing the quality, observance of time and cost objectives as well as documentation. In view of the specific boundary conditions sufficient time must be allowed for that, people affected must be heared. For variations, alterations corresponding administrative, technical and contractual precautions must be taken.

Apart from that the implementation of the measures in agreement with the people affected is of central importance. Conditions are:

- accepting the minimization of the burden on people affected (emissions, duration, time) as essential criterion apart from costs and administrative requirements,
- detailed discussion of remediation plannings with people affected, if necessary, participation already in the planning phase (individual discussions, small groups),
- joint determination of detailed regulations for the remediation measures,
- transparency at the allocation of tasks and competences, continuous availability of corresponding contact partners,
- maintenance of good (also technically good) communication structures.

3 History of the site

In the course of the National Socialist armament program the Supreme Command of the Armed Forces (hist. Wehrmacht) in 1938 determined the south of the small village Allendorf in the administrative district Marburg-Biedenkopf to be the location for two factories producing explosives:

- The factory Allendorf, planned and built by the Dynamit AG (DAG, with 61% I.G. Farben) and operated by a subsidiary of the DAG, the Verwertchemie. Owner and proprietor of the factory was the company Montan Industrie GmbH owned by the German Reich.

- The factory Herrenwald planned and built the Westfälisch-Anhaltische Sprengstoff-AG (WASAG, also I.G. Farben by majority) at the expense of the navy, of which it leased the finished equipments for production.

After 1938 the biggest TNT (trinitrotoluene) production plant of the German munitions production was established in Allendorf. Until the factory was closed down on the 27th of March 1945 approx. 130,000 tons raw-trinitrotoluene (TNT) were produced in the DAG and manufactured into bomb and grenade fillings. In the factory Herrenwald approx. 100,000 tons explosives were filled up.

Both factory sites comprise approx. 400 ha each. In the DAG totally 430 massive buildings and factory halls were erected for production. For reasons of camouflage their roofs were planted with greenery. Moreover approx. 60 km in-plant sewage installations and a 24 km long sewer leading into the river Lahn were in use for the up to 6000 m³ highly toxic liquid waste per day.

From 1945 - 1948 parts of the installations of this former explosives factory were used for taking ammunition from German and American stocks out of the laboratories. More than 17,000 tons ammunition were taken out of the laboratories, decomposend and caused to detonate. The technical installations were dismounted and approx. 30 % of the buildings were destroyed by detonation during dismounting work.

Today the area shows a distinct mixed utilization between private housing and commercial/industrial areas. As commercial and industrial location the DAG-area is of regional importance. Apart from that derelict land is also found. Today more than 4000 of the 21,000 inhabitants of Stadtallendorf live on properties that once was used for the production of explosives, more than 8000 people work in factories, which have been established on such grounds. The current road network widely corresponds to the 25 km of former roads and cart tracks.

Nearly 50 % of the former in-plant sewage system are used for the public sewage removal. The existing infrastructure of the waterworks of the DAG has been integrated into the regional drinking water supply. Annually approx. 11 mio. m³ are provided by the waterworks Stadtallendorf.

4 RISKS

The production and processing of explosives as well as dismounting the installations in the post-war phase caused contamination of soil and groundwater. Redistribution of contaminants were caused by extensive construction measures of civil reutilization of the site after 1948. Questions concerning possible health risks, which could be caused by residues of the explosives production, had not been asked for a long time.

Since the end of the Seventies the groundwater situation was investigated first. Initial analyses for discovering, detecting and evaluating contaminated areas were carried out in 1988 on behalf of the regional council Gießen. Since 1990 an extensive systematic investigationl program has been run in different working steps (historical investigations, sampling, location-specificinvestigation).

Result of the analyses and their evaluation is that the DAG-site has been burdened with contaminants in such a heavy way that a risk for human health cannot be excluded. Especially via the soil (eating cultivated foodstuffs) the conaminants can reach the human beings and damage their health. A long-term, effective remediation is therefore necessary. For minimizing the exposition the district public health department gave recommendations for action and utilization. If these recommendations are observed, no short-term risks exist for even sensitive persons.

5 REMEDIATION CONCEPT

During the course of the development of the remediation concept it has turned out that there is an area of conflict between the „utilization-related remediation", on the one hand, and „groundwater-related

remediation", on the other hand. The scope of remediation in the field of groundwater protection exerts a considerable influence on all aspects of the process from investigation to remediation. Apart from that it essentially determines the time needed for the remediation and the costs in connection.

In case of the purely utilization-related remediation of soil the upper contaminated soil horizons are remediated in partial areas to a different extent so that the individual utilization is secured. The rest of the contaminants remains in the soil. The penetration of contaminants into the groundwater to be expected is prevented from further distribution by hydraulic extraction.

A soil remediation purely related to groundwater in its depth and surface widely exceeds the utilization-related remediation. To carry out precautionary groundwater protection within the DAG-site, in the extreme case, means that independently of the utilization all contaminants in the subsoil, i. e. in loose rock and solid rock, are removed. The compatibility of such remediation measures with existing utilizations is very problematic.

The remediation measures mainly refer to the elemination of health risks by contaminants in soil and groundwater. The remediation measures are utilization-related and ecologically harmless. Groundwater protection is of special importance. The remediation is economically justifiable, and the use of public funds takes palce economically and goal directed.

The remediation strategy for the environmental media soil and groundwater contains the following main characteristics:

- The remediation is carried out according to the utilization requirements, i. e. in view of the current and future utilization of the location.
- For the remediation of soil levels relevant to utilization an excavation of soil is planned for residential area sites. In the area of industrial-commercial utilization and of traffic areas measures as sealing and utilization restrictions have been planned.
- Apart from a utilization-related remediation– with regard to groundwater protection – a remediation of deeper soil layers below the utilization-relevant layers has been planned.
- One of the biggest hot spots for the groundwater is the Tri-Halde. In view of the inhabited surfaces urgently to be remediated the remediation is, however, deferred for the time being.
- Owing to the fact that a complete extraction/remediation of the soil has not been planned and is partly impossible, an hydraulic extraction of groundwater on the DAG site, protecting the drinking water, is carried out.
- Together with the remediation of soil at hot spots the local and extended hydraulic measures are so intensively carried out that drinking water from the lower groundwater level remains uninfluenced. The procurement of drinking water from the drinking water wells is cleary separated from the hydraulic extraction.

6 Soil

The investigation of the soil contamination took place by the determination and historical investigation of warfare-related contaminations and suspicious areas as well as examinations within a grid of 50 x 50.

The investigationl of the soil contamination first aimed at the areas close to the surface relevant for utilization. It was not the aim of the analyses, to investigate the total area of the loose rock to the grown soil or bed rock.

Within the grid the total former DAG-site was investigated. The examination depth normally was 2.0 m. Here contaminations with nitro aromatic compounds were found on considerable parts of the surface.

The results of the site investigationl to a large degree proove the results of the historic investigation as well as the other examinations. The examination depth went down to 4.5 m. Contamination hot spots, in particular surface contaminations, were found in the areas of the former TNT-production chains. The supplementation and completion of the investigationl of the soil contaminations could be finished in 1997 to a large degree.

6.1 Test site

In order to collect experiences with the remediation for subsequent remediation measures in other partial areas of remediation with partly sensitive private housing utilizations, a first uninhabited area of remediation was determined as a test site for soil remediation.

The property has got a size of in total approx. 5,000 m² and was commercially used. The surroundings are used for commerial purposes and private housing. The former utilization of the test site consisted of buildings of the TNT-production and a settling basin. The thickness of loose rock is approx. 2 to 8 m. The groundwater level is deeper than 35 m below ground level. The test site is within the area of the extended hydraulic extraction. Before, during and after the remediation of the area an intensive groundwater-monitoring takes place.

By the excavation to a depth of 9 m below the ground level of approx. 11,000 tons soil in need of remediation approx. 9 tons explosive-specific compositions could be removed. After finishing the remediation the site can be utilized for private housing.

For the systematic collection and evaluation of information for the improvement of planning and implementation of further remediation measures the remediation of the test site was accompanied by a test program.

The test program was carried out independently of the „normal" tasks at a remediation measure eg. process planning, site management and expertise as regards the remediation/quality assurance and should allow an uninfluenced test. The test program deals with the following facts:

- meaningfulness of existing investigationl results owing to actual facts,
- realization of the specifications of the remediation conception and remediation planning
- effects of concrete individual measures on human beings and environment,
- partial quantities, stock logistics, mass evaluation and documentation,
- comparison of the analytics at different samplings and with soil valuation,
- quality assurance regarding the remediation success,
- groundwater monitoring in the environment of the test site,
- investigationl and judgement of the organization, communication and decision structures and the time management.

6.2 Remediation process

First activities in extensive contaminated soil remediation has been taking place since 1997 in a first remediation area. Here remediation activities take place until March/April 1998 on properties of 10 owners, 5 of them used for private housing. The remediation process is divided in the phases outlined in the following:

After analysing the soil and evaluating the soil contamination the regional authorities decide, whether the public welfare is considerably affected by the corresponding property. If this is the case, the property is determined as contaminated site. Before the determination the proprietors are informed and heard by the regional authorities.

The determination of a contaminated site takes place on the basis of a documentation, which contains all relevant information (historical utilization, analyses carried out, contaminations found) and is in hands of the owner of the property as well as of the authorities.

Groups of properties, which must be remediated, are combined to remediation areas. Here in particular process-related, logistic reflections play an important part. For a remediation area a remediation plan is made out. The regional authorities determine remediation objectives for each property.

On that basis an approval planning is prepared by an engineer's office, which shows all technical and organizational facts and measures essential for carrying out the remediation. Part of this is also the balancing required by conservation of nature and forest laws.

In the course of the preparation of the plan an information is given to the proprietors, users and residents. With the presentation of the remediation plan approval procedure is started.

The remediation-approval procedure is carried out by the regional authorities according to the regulations of the Hessian Contaminated site Law. With the approval procedure for the remediation plan it is to be guaranteed that the areas after finishing the remediation do not represent any risk for limb and health of the human being as well as no risk for the environment in connection with the existing or planned utilization of the area (§ 1 HAltlastG) and at carrying out the remediation measures an impairment of the public welfare is avoided (§1 H AltlastG).

In the remediation plan approval procedure for the warfare-related contaminated site Stadtallendorf a participation of the public and the people affected is taking place. The proprietors and users affected are heard and have got the right to inspect the records. The public is informed by opening the planning records to the public (2 weeks). There is the possibility, to raise objections. Two weeks after the end of the objection period a discussion is carried out by the regional authorities together with those raising the objections. Subsequently the final examination by the regional council under consideration of the results of discussion and the official statement takes place.

In parallel to the planning the preservation of evidence and inventory of the remediation areas takes place. The property inventory (buildings eg. summer houses, patios, other things as fences, walls, etc. the plants of the garden) are surveyed and the inventory is taken. The inventory and evaluation is part of the remediation agreement, which is made between the regional council and the owner of the property and refers to legal, financial and organizational aspects of the remediation.

After the approval of the remediation plan the detailed engineering process planning with subsequent invitation to tender and award of building work contracts is taking place. The tender is made in public.

Carrying out the remediation starts with the building site equipment on the remediation area (black-and-white installation, office, laboratory, discharge station for soil excavation, equipment of a sampling and reinstallation stock, erection of hoardings).

The remediation areas are cleared, i. e. the vegetation, movable buildings eg. summer houses, etc., fences and walls are removed, provisional access roads to the property are built.

The excavation of soil takes place in depth steps of 1 m. In remediation areas with exclusively utilization-related soil contamination the soil is excavated with diggers to 1 m depths. At known high soil contaminations and foreseeable gaseous emissions the excavation is made below a tent hall. Tents apart from that prevent the penetration of rain water and with that the mobilization of contaminants.

In remediation areas with hot spots relevant for the groundwater the soil is excavated to a max. 3 m depth, if possible regarding engineering and financially in proportion. Special measures are used, if the location of excavations endangers the stability of buildings.

Excavation is carried out by using commercially available devices of civil engineering. Supplementary worker's protective equipment are active-carbon-filters and bullet-proof glass panes). The special local conditions (work under confined conditions, standstills because of sampling, analytics and release, dense network of known and unexpectedly appearing pipes) restrict the average daily excavation and transport capacity to 100 m^3 per building site.

Sampling of the bottom area and the wall areas of the excavation serves the examination of the remediation success in the depth and in the area. If values are found out to be exceeded, the excavation measures are continued. The so-called recutting of bottom and lateral areas exceeding the extent known from the investigationl renders costs as well as duration of the remediation only partially calculable.

The excavated soil is subdivided into 5 categories according to its contamination level (mg TNT-TE/kg). Not clearly classifiable soil is transported into the sampling stock located in the remediation area, samples are taken, analyzed and classified into one of the five categories. With the classification it is decided, whether the soil is cleaned in a soil treatment installation, or can be utilized or whether it can be reinstalled immediately. The reinstallation of soil takes place according to the different utilization purposes. Apart from quality requirements the reinstallation soil must also meet soil-mechanical requirements (e.g. compacting capacity)

The expertise accompanying the remediation and the quality assurance controls and documents the total remediation measure and the remediation success (achieving the remediation goal). The results of individual excavation sections are conveyed to the regional council Gießen, who on that basis gives order to release filling in or „recutting".

Contaminated soil > 80 mg TNT-TE/kg is transported by rail to a off-site soil treatment plant, where it is cleaned. The cleaned soil is partly retransported to the site and reinstalled there, partially it is externally utilized.

Handling the soil, (but also rubble, organic materials and explosives removed from the soil) is controlled by a „soil management coordinator", the tasks of which comprise the adaptation of the operation as well as the storage and removal with operator admission, invitaiton to tender and site management of crushing, riddling, organization of transport services, documentation of the material flows and investigation, price inquiry of disposal.

After finishing the soil exchange the remediation areas are restored or recultivated, i. e. gardens are restored according to the inventory taking.

The cancellation of the determination of a contamined site takes place by the regional authorities, when the remediation measure has been carried out and the determined remediation goal has been achieved.

BLOW OUT OF TRECATE 24 CRUDE OIL WELL: HOW BIOREMEDIATION TECHNIQUES ARE SOLVING A MAJOR ENVIRONMENTAL EMERGENCY IN A VALUABLE AGRICULTURAL AREA

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Key words: authorities' role, bio-piles, biological treatment, bioremediation, contaminated soil, hydrocarbons, in-situ bioremediation, on-site treatments, PAH, removal rates.

SUMMARY

On February 28th, 1994, a blow-out occurred, while drilling the crude oil well TR 24 in the Trecate-Villafortuna oil field (Northern Italy). The blow-out casued the release to the environment of the following estimated volumes of fluids: 12,600 m^3 of crude oil, 1,000,000 m^3 of gas, 1,000 m^3 of water. The fall-out of crude oil affected approximately 1500 ha of intensely cultivated agricultural soil. As soon as the blow-out ceased, after 36 hours of uncontrollable release, AGIP entrusted the Battelle Institute (Geneva) with the preparation of the environmental monitoring and reclamation plans. The reclamation plan was based upon different on-site bioremediation techniques, both *in-situ* and *es-situ*; the fully implemented project has been prepared and is being implemented by Foster Wheeler Environmental. This paper describes the principles of the techniques adopted for the complete bioremediation of both the surficial soil (pollution ranging from 50 mg/kg to more than 50,000 mg/kg total petroleum hydrocarbons) and subsoil, as well as the engineering and design of the bioremediation systems. The results of two years of operation are also reported and commented, with specific attention to TPH and PAH removals. *In situ* techniques include landfarming, bioventing and enhanced vacuum recovery for free-phase hydrocarbons. The biobile technique was adopted for the *ex situ* remediation of the highly polluted soil; two engineered biopiles, 15.000 m^3 each, were designed, built and operated.

Contaminated Soil '98, Thomas Telford, London, 1998, 403–412

1. The incident

On February, 28th, 1994, at 3.15 pm, the well TR 24 of the Trecate-Villafortuna field suffered a blow out.

The incident happened when drilling of the TR 24 had already reached its first objective, at a depth of 5,600 m, while attempting to control a "kick": after closing the B.O.P. (pipe rams) a drill pipe rupted above the rig floor and the formation fluids started blowing out without any possibility of control.

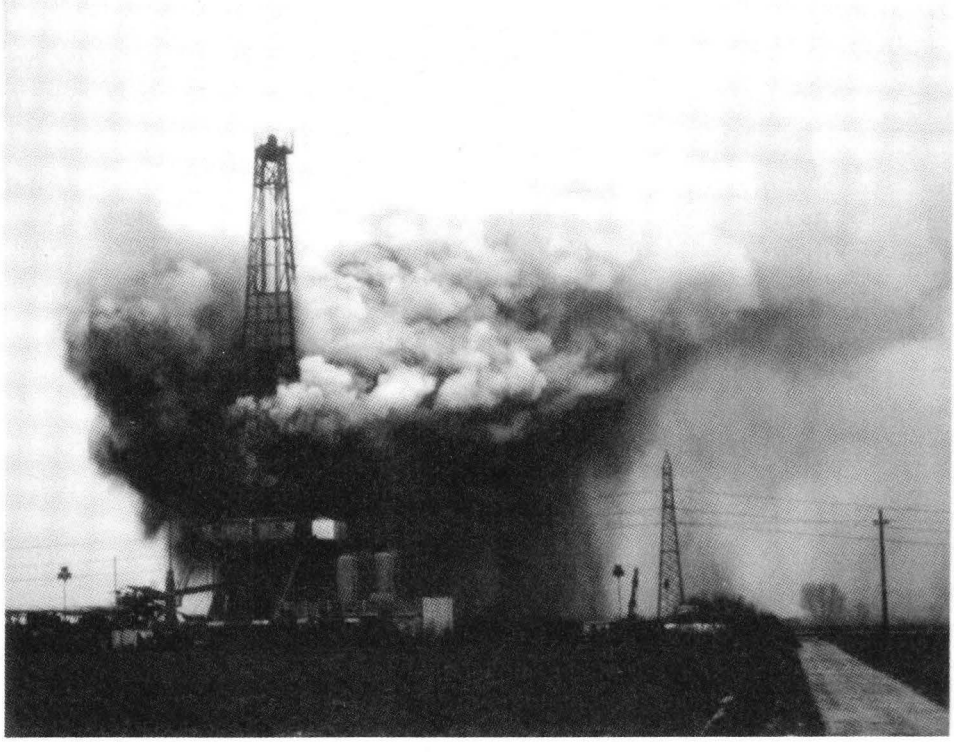
The fluids did not ignite and the fall-out plume extended downwind, up to a distance of 2 km and more, reaching the town of Trecate and the National Road n. 11.

On March 2nd , at 3 in the night, after almost 36 hours of uncontrolled eruption, the blow-out ceased spontaneously, due to downhole formation collapse and debris plugging.

The estimated amount of fluids erupted from the TR 24 are as follows:

- 12,600 m^3 of oil (or 80,000 bbls);
- 1,000,000 $S.m^3$ of gas (or 37 M Scf.);
- 1,000 m^3 of formation water.

The most part of the liquids impacted the fields within a radius of 600 m downwind; no significant fall-out took place upwind.



"Figure 1 - The incident"

2. Characteristics of the impacted area

In the area where the TR 24 well was located agriculture is the principal activity, mainly devoted to rice cultivation. The rice fields show a typical morphological arrangement, with level ground surrounded by bounds having little elevation and a complicate network of irrigation ditches deriving from main canals; as the rice cultivation needs the fields to be kept flooded, the soil in such fields has a low superficial permeability.

At the time of the incident the irrigation system was dry, except for the main canal, where a reduced flow was maintened; the Irrigation Authority was immediately requested to shut down the canal in order ot avoid the oil fo flow downstream, causing additional pollution.

No natural stream is present in the impacted area, the valley of Ticino being around 3 km eastward, outsite the limit of the fall-out plume; also the artificial ponds, related with gravel excavation, where the water table comes at the surface, were not contaminated by oil.

3. Clean-up activities

The clean-up operations started immediately after the end of the blow-out; the oil which had flooded the rice fields was recovered by suction; 9,350 m^3 of oil were recovered in such a way.

The streets. pavements and houses in the town of Trecate were cleaned up by employing up to 500 workers during several weeks; the superficial soil and/or green, in gardens and orchards, was removed and replaced.

The main irrigation canal was cleaned up by means of pressure water and steam cleaners, in order to allow the irrigation to start in time for the agricoltural season; the sewage system was purged in order to avoid the oil to reach the municiapl sewage treatment plant.

4. Environmental monitoring and restoration

On March 2nd, AGIP entrusted the European Section of the Battelle Memorial Institute, in Geneva, with the preparation of an Environmental Monitoring Plan and a Remediation Project aiming to both evalutate the environmental consequences of the incident and to grant the prompt recovery of the existing agricoltural context, as urgently requested by the Authorities.

4.1 Monitoring Plan

The Mnitoring Plan, first presented on Marc 15th, and implemented according to the Authorities' requests, was conceived for monitoring all the environmental domains actually or potentially affected by the event; its main features are as follows:

- Soil pollution monitoring, through 220 sampling points for the TPH and PAH content and its evolution with time ; (Frequency: every 3 months)
- Surface water pollution monitoring, through 27 sampling points; (frequency: monthly)
- Groundwater pollution monitoring: 30 sampling points; (frequency: monthly)
- Air pollution monitoring, through 8 stations (reduced to 4 after 3 months) for the continuous monitoring of: THC; CH_4, SO_2; NOx and O_3, together with atmospheric conditions;
- Biological effects on plants and wildlife, through sampling and capture campaings, twice a year.

Up to present, the decrease of TPH and PAH content in soil, as a consequence of bioremediation efforts, has been monitored through 13 sampling campaigns; no pollution of both groudwater and surface streams has been detected outside the most polluted area;

the air pollution always remained within the limits, except for the first ten days after the incident.
The effects on plants and crops have been studied by both the Agricolture Department of the Regione Piemonte and Battelle, through green-house and open field tests, showing no significant alteration, either qualitative or quantitative, in rice grown on polluted soil compararively to current rice.
Monitoring of flora and wild-life, which require a longer observation time, although still being evaluated, show a substantial recovery.

4.2 Remediation Project

The area impacted by the blow-out is mainly devoted to agriculture and has been producing high quality rice crops for more than a century. Therefore, the basic request advanced by the Authorities and the farmers' associations was for a Remediation Project which could avoid any alteration of the agricoltural context. Since the rice fields in the area have a peculiar, quite thin (0.5 m) level of loamy soil, which is of basic importance for its texture, composition and water holding capacity, the remediation project was mainly based upon *is situ* bioremediation. Preliminary identification of the existing bacterial strains in the polluted soil and relevant aptitude to hydrocarbon degradation had been carried out, as well as treatibility tests, at laboratory scale, which confirmed the degradation to be possible by means of the native bacteria. Also for the most polluted areas, the same principle of bioremediation by means fo the native bacteria was adopted for *ex situ* (but still "on site") bioremediation of the soil in "biopiles", after having scraped out from the fields the most superificial (and most polluted) layers of soil.
Based on the above considerations, the Remediation Project for the superficial soil provides the following:

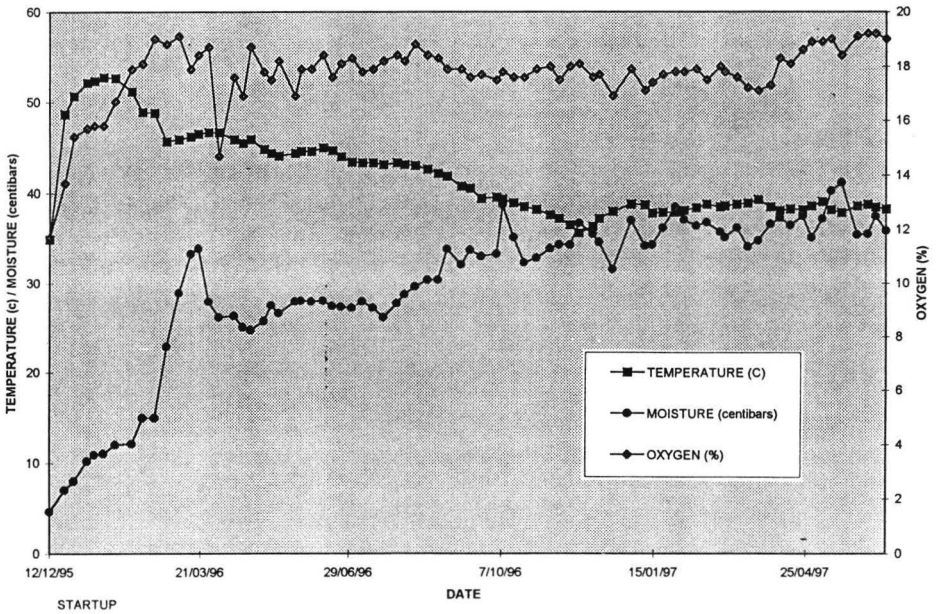
- Preliminary suction of all the residual liquid oil and water from the flooded fields;
- Remediation efforts graduated according 3 different zones:
  zone 1 - very slightly polluted (<50 mg of total hydrocarbons per kg of soil) - monitoring of the natural degradation with the usual agricoltural practise.
  zone 2 - pollution between 50 and 10,000 mg/kg - gradual land-farming, according to the different degrees of pollution; no crops allowed in order to replicate the land farming with the required frequency.
  zone 3 - pollution above 10,000 mg/kg - intensive land-farming; in the most polluted areas (about 13 hectares) the soil is removed and treated in "biopiles" in order to optimise the biodegradation of the hydrocarbons.
  Almost 30,000 cu. m of soil were scraped off and treated in such a way.
- Remediation of subsoil (pollution was detected early in 1995) by applying bioventing and phase separated hydrocarbons vacuum enhanced recovery.

On the basis of such a preliminary plan, AGIP issued an international bid for a fully implemented bioremediation project. The selected project, prepared by Foster Wheeler Environmental was finally approved by the Authorities in October 1994. The estimated duration of the reclamation project was about 3 years; the recovered areas were to be given back to the owners for current agricoltural operations.
The first results, after the first six months of remediation through land-farming, proved to be very satisfactory: more than 85% of the affected area (97% of the area initially

interdicted by Authorities) was recovered and given back to the farmers in February 1995, before the beginning of the rice campaign; further areas were released in January 1996.

Biopiles

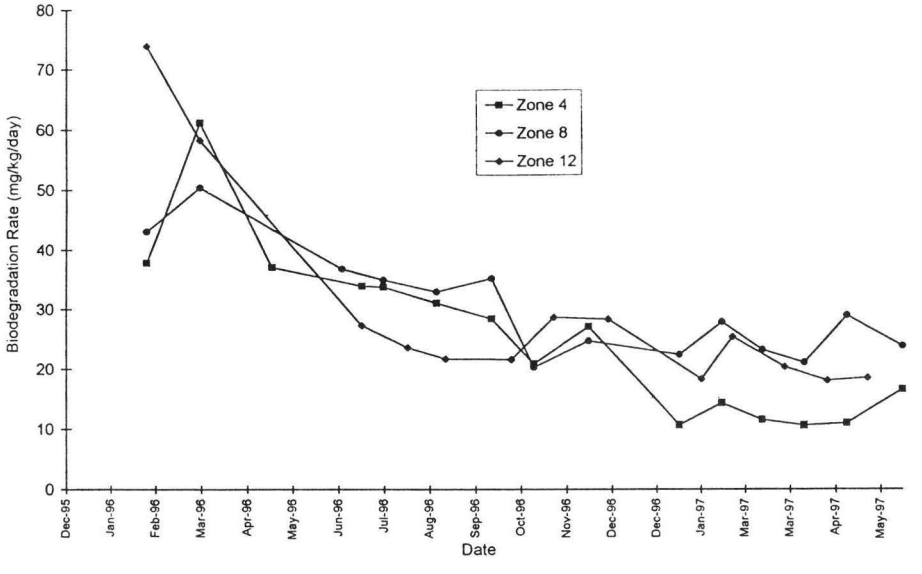
Two biopiles were constructed, to contain respectively 15.000 m^3 and 12.000 m^3 of unbulked soil (average contamination ranging between 10,000 and 20,000 mg/kg), additioned with 20% of low-resin wood chips as bulking agent, in order to improve the air permeability. The biopiles were designed to achieve the lowest possible residual hydrocarbon endpoint concentrations and to reach those endpoint concentrations in the shortest possible time.To achieve these objectives, the biopiles were designed and constructed in a manner that provided for control of the process parameters that have the greatest potential to impact the rate of biodegradation (i.e., oxygen concentration, moisture content, and temperature). The biopiles were constructed atop an impermeable liner and a permeable base material that were designed on a zone and lift basis. There are eleven lateral zones in each biopile and six vertical lifts in each zone. Air injection pipes are found on the surface of lifts 1, 2, 3, 4 and 5. Moisture addition lines are found on the suface of lifts 1, 3 and 5. Heat trace elements are found on the surface of lifts 1, 2, 3, 4 and 5. The rates of air injection, moisture and nutrient addition, and heat trace operation are controlled through a computer based system that includes several local processing units (LPU). Moisture sensors, resistance temperature detectors (RTD), and soil-vapor sampling devices were installed at 136 locations in each biopile. These were interfaced with a computer based sampling system and programmable logic controller (PLC) and were used to determine moisture, temperature, oxygen, carbon dioxide, and total volatile hydrocarbon concentrations within the biopiles. Figure 2 shows representative biopile monitoring data .



"Figure 2 - Average process control data summary for biopiles"

Examination of the data in Figure 2 shows that the oxygen concentration was near 0% at the time of system startup and very rapidly increased to about 20% as a result of air injection at a rate of approximately 34 m^3/min by two high volume centrifugal blowers. The data also show that the temperature has been maintained at a near optimal 40 to 45 °C and that soil tension has been maintained between 40 and 50-cB, wchich corresponds to a near oprimum moisture content fo 15 to 25%. In addition to the process control parameters, which were monitored daily, the rates of biodegradation were measured peridically through *in situ* respiration testing. In this process, air injection is suspended and the rate of oxygen decay is measured as a function of time.

Monitoring biodegradation rates as a function of time provides a tool by which soil cleanup progress can be assessed. Prior to initiation of biopile operation, a short duration pilot test was run to estimate the initial biodegradation rate. Results of this test revealed a rate of nearly 200 mg/kg/day. However, over the course of biopile operation, the mass of hydrocarbon has decreased. Because the biodegradation process is substrate limited, a decrease in rate was expected as the hydrocarbon mass decreased. Figure 3 shows the observed in situ biodegradation rates as a function of time since biopile startup.



"Figure 3 - Average respiration rates data summary for biopiles"

In addition to the *in situ* respiration testing, biopile progress was also monitored through a program of quarterly soil sampling. At the end of each quarter of biopile operation, soil sampling were collected from approximately 100 pretedermined multi-depth sampling locations in each biopile. The concentration of total petroleum hydrocarbon (TPH) was determined via dichloromethane extraction and quantitation via gas chromatography with a hydrogen flame ionization detector. These data were used with the *in situ* respiration data to assess biopile operation.

The two biopiles were started up on 24.11.1995 and 07.12.1995, respectively; as described, the hydrocarbon degradation was monitored by both respiration tests and quarterly sampling: after six months, the average degradation levels attained were 48% for biopile 2

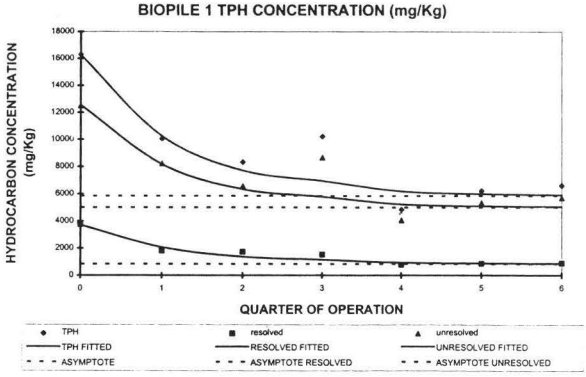
(10,000 mg/kg original average concentration as TPH) and over 60% for biopile 1 (20,000 mg/kg). Degradation rates as high as 60 mg/kg per day were measured through the respiration tests in good accordance with the analytical results. Remediation effectiveness was monitored following the decrease of total petroleum hydrocarbons (TPHs) and polycylic aromatic hydrocarbons (PAHs). Additionally, the formation of several classes of petrleum metabolites were tracked over time to assist in mass balance calculations and ecological and human health risk assessment of the remediated soil.

After 18 months, after the formation of a variable "hump" of unresolved metabolites had been observed, comprised of three major classes of compounds (keytones, aldehydes, and, mainly, carboxylic acids) the residual hydrocarbon content, calculated on the basis of "peak to peak" integration, was around 5% of the original oil, as shown in figure 4.

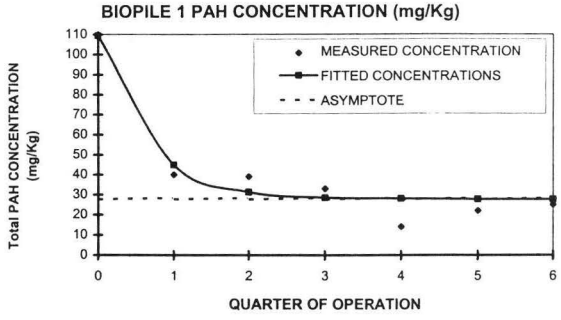
The reduction of PAH content was also observed up to 4-rings PAHs, as shown by figure 5.

Based on these results and the risk assessment performed, considering the exposure of potential human targets (farmers and inhabitants), Authorities finally granted their authorization to redistributing the treated soil on the fields of provenance, to continue bioremediation through less intensive treatment, such as land farming.

This is the first case in Italy of acceptance of the successful results of treatment of oil polluted soil in biopiles.



"Figure 4 - Reduction of TPH concentration vs time"



"Figure 5 -Reduction of PAH concentrations vs time"

Landfarming

Some residual hydrocarbon remained in fine grained surficial soils following excavation. In keeping with the desire to utilize bioremediation approaches exclusively to address the spilled crude oil, these soils were treated via landfarming. The implemented approach was generally consistent with traditional applications of this technique. That is, it was assumed that the primary fate mechanism would be biodegradation and that the primary limiting factor controlling the process would be oxygen concentration. Thus, the soils were disrupted via plowing and tilling to increase the rate of aeration relative to that which would be possible through diffusion alone. Nitrogen and phosphorus were also added in the form of conventional agricultural fertilizer to ensure that the bioavailability of these macronutrients did not become rate limiting.

In order to render the process as efficient and cost effective as possible, oxygen probes were installed in the landfarmed area. These probes were interfaced with micro-dataloggers which were used to document oxygen concentration in the soil as a function of time. The sensors were polled weekly to determine those areas in which the oxygen concentration had decreased to a point that would limit the rate of aerobic biodegradation (i.e., less than 5%). This monitoring program insured that the area was plowed or tilled only when needed, thereby eliminating wasted effort and capital expenditure.

Landfarming has been very successful and has reduced surficial soil TPH concentrations from in excess of 10,000 mg/kg to approximately 50 mg/kg, the designated target cleanup level.

5. Subsoil contamination

Despite the low permeability of the superficial soil of the rice fields some contamination has been detected in the subsoil after scraping the fields. In addition, due to the presence in the fields of a number of drainage pits, normally used for drying the fields before the harvesting, the floating oil in the most polluted area had the possibility to seep into the subsoil before the urgent clean up intervention could stop the infiltration.

After a preliminary soil gas survey campaign, an extensive program of soil and soil gas sampling was carried out by means of "Geoprobe^{TM}" apparatus, in order to assess the subsoil contamination conditions. The contamination was found to be patchy distributed, both in horizontal and vertical dimension, with hot spots of highly contaminated soil and, possibly, a phase separated hydrocarbons (PSH) lens floating on top of the water table. Phase separated hydrocarbons were actually detected on the water table during the minimum level period (November through March): a tentative estimate of the PSH volume, using the thickness observed in some of the piezometers installed in the area, corrected for both the specific gravity and interfacial pressure amounted to some 400 m^3.

Despite the presence of PSH and the seasonal fluctuation in water table level (about 5 m, linked to irrigation period), no detectable dissolved phase plume was observed in the groundwater monitoring network of piezometers. Such an evidence has been interpreted as a result of the very low solubility of the oil components, coupled with intrinsic bioattenutation, via aerobic and anaerobic bacterial degradation. The phenomenon has been monitored and attempts are presently carried out for its modelling.

Remediation activities of subsoil made use of bioventing and PSH recovery, as described hereinafter.

Bioventing

The crude oil impacted vadose zone encompasses an area of approximately 12.5 ha. Because the area surrounding the site is used almost exclusively to cultivate rice, the water table, and thus the vadose zone thickness, is highly variable over the course of a year. During the period when there is no irrigation, the vadose zone is approximately 12.5-m thick. In contrast, during the period when the rice fields are irrigated, the vadose zone may be as thin as 6.5-m. Due to the nature of the vadose soils (i.e., coarse grained sand and gravel) the extent of capillary rise within the vadose zone is negligible. At the time of the oil well blowout, the water table was near its deepest point and thus, the vadose zone was near its maximum thickness.

Given the large area and soil volume that required remediation, it was determined that bioventing would be a feasible remediation tool. Bioventing is an *in situ* approach in which indigenous microorganisms are used to mineralize petroleum hydrocarbons using oxygen as the teminal metabolic electron acceptor. Its objective is to prevent oxygen from becoming a limiting factor in aerobic respiration by injecting ambient air into the subsurface. Experience has shown that, in most instances, the availability of macronutrients such as nitrogen and phosphorus does not limit hydrocarbon mineralization.

A pilot test was carried out to generate the data needed to design a bioventing system for the site. Design parameters determined through this field effort included the radius of air injection influence (i.e., the area of remediation defined by an induced oxygen concentration sufficient to support aerobic biodegradation), quantification of pressure/airflow relationships, the *in situ* biodegradation rate, oxygen demand, and the optimal air injection rate. Based on the results of this pilot test, a bioventing system was designed to address the entire 12.5-ha area to a depth of approximately 12.5-m. The system included 26 air injection wells, five air injection pump stations, associated air delivery piping, and 36 *in situ* soil-vapor monitoring clusters.

Prior to initiation of system operation, the entire impacted area was nearly devoid of oxygen (less than 5%) and the average estimated biodegradation rate was approximately 5 mg/kg/day. Within about two weeks of system initiation, the oxygen concentration over the entire impacted area increased to nearly 20% and the biodegradation rates began to increase slowly. By the end of the first quarter of operation, the biodegradation rate had increased to as high as 10 mg/kg/day. By the end of the second quarter of operation, biodegradation rates as high as 80 mg/kg/day were observed. It is believed that, due to the relatively short time between oil introduction into the subsurface and initiation of bioventing, the initial microbial biomass was small. Over the course of operation, it is likely that the biomass acclimated and grew considerably, which resulted in the dramatic increase in observed biodegradation rates.

Phase Separated Hydrocarbon Recovery

Several approaches to vacuum-enhanced multi-phase extraction were evaluated, including bioslurping, In bioslurping, vacuum is applied to a recovery well to enhance the rate of oil recharge into the well and the accumulated oil is extracted via air entrainment or direct suction. Application of the vacuum not only improves the rate of oil recharge in the well, but also serves to distribute air (both that which may be injected through bioventing and air infiltrating from the surface), thereby increasing the availability oxygen and enhancing biological activity in the vadose zone. A pilot test was carried out to evaluate oil recovery options and to generate the data needed to design a full scale recovery system. The pilot test evaluated conventional pumping without vacuum enhancement, vacuum enhanced

pumping, and vacuum enhanced fluid entrainment. Results of the test showed that vacuum enhancement improved the rate of oil recovery by a factor greater than three relative to no enhancement. It also showed that, at this site, vacuum enhanced recovery and extraction with a hydrocarbon/water separating downhole pump was superior to air entrainment alone (i.e., using an above ground-pump and a drop tube). Based on these data, a vacuum enhanced recovery system was developed that includes one vacuum source and five extraction points.

6. Conclusions

As a consequence of the blow-out that occurred in the course of drilling the oil well TR 24 in norhen Italy, an area of about 500 hectares of rice production land was impacted by a large amount of light crude oil.

After the emergency actions and the urgent clean-up activities had been started, an environmental monitoring plan was conceived, extended to all the environmental components.

A reclamation project was then issued, based on bioremediation of the polluted soil by meand of the native bacteria. The remediation effort was gruaduated as a function of the pollution degree: landfarming (*in situ)* is applied to soil showing a contamination ranging between 50 and 10,000 mg/kg, while the excavated superificial soil of the most polluted area (up to more than 50,000 mg/kg) is treated *ex situ* in two biopiles, 12,000 and 15,000 m^3 of unbulked soil, respectively.

Subsoil pollution is addressed via *in situ* techniques, such as bioventing of the vadose zone, while vacuum enhanced recovery of PSH is carried out on the water table. The applied methods have proved to be effective as more than 90% of the polluted fields (and more than 98% of the area originally interdicted by the Authorities) have been released to agriculture 23 months after the incident. The degradation rates, observed in both the biopiles and in the subsoil after bioventing has been initiated, show a very high potentially for the methods of bioreclamation for soils polluted by petroleum hydrocarbons.

A CASE STUDY OF THE REMEDIATION OF CHLORINATED HYDROCARBON CONTAMINATION USING DUAL-PHASE VAPOUR EXTRACTION

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Key words: clay, contaminated plume, degradation, groundwater clean-up, halogenated hydrocarbons, PAH, soil vapour extraction, solvents, vacuum extraction

SUMMARY

A dual-phase vapour extraction system has been utilised for the remediation of historical spills of waste degreasing solvents utilising the 'slurper' method, at a site comprising fine clayey soils and glacial tills. The remediation project is on-going and the paper describes the experience gained from an innovative site investigation technique, the extension of the remediation area to cover secondary source and the progress of contaminant removal to date.

KURZFASSUNG

Für die Sanierung von historischen Überlaufschäden, verursacht durch Entfetter-Lösungen, wird ein zweiphasig arbeitendenes Bodenluft-Absaugsystem nach der "Slurper"-Methode angewandt. Der Boden des zu sanierenden Grundstücks besteht aus feinkörnigen Lockersedimenten und glazialen Geschiebelehmen. Eine das laufende Sanierungsprojekt begleitende Studie beschreibt die Erfahrungen, die aus der Anwendung einer innovativen Untersuchungstechnik gewonnen wurden. Ferner wird über die Erweiterung der zu sanierenden Fläche mit einer zweiter Eintragsstelle und über den Fortgang der Sanierung berichtet.

RÉSUMÉ

Un système d'extraction de vapeurs "double-phase" a été utilisé pour le rémédiation des fuites anciennes de dissolvants de dégraissage, en utilisant le méthode 'slurper', à un chantier comprenant des sols fins et des argiles d'origine glaciale. Ce projet de rémédiation est actif à l'heure actuelle et cette conference a pour but d'examiner les résultats obtenus à partir de cette technique d'investigation innovative, du développement de la zone du rémédiation pour inclure une source secondaire et également pour examiner l'efficacité du nettoyage des contaminants jusqu'à l'heure actuelle.

Contaminated Soil '98, Thomas Telford, London, 1998, 413–424

INTRODUCTION

There are few published examples on the treatment of dense non-aqueous phase liquids (DNAPLs) such as chlorinated solvents. The risk from these liquids is that being heavier than water they can penetrate the ground below the water table.[1,2]

This remediation project, current at preparation of this paper, includes the following aspects:

1 In addition to the volatile contaminants, there are also semi-volatile compounds such as polyaromatic hydrocarbons (PAHs) and phthalates, the latter having particularly low volatilities. The chosen remediation programme relies on a dual-phase vapour extraction system and the bio-degradation of these low volatility compounds, once they are released from solution in the more-volatile compounds, after the more-volatile compounds are stripped and removed from the ground.

2 The glacial geology of the superficial deposits at the site is relatively complex and includes a mixture of silty sand, low permeability clays and an underlying sandy gravel layer.

3 There is a pronounced downward hydraulic gradient as a result of historical water abstraction from the basal Chalk aquifer.

4 After commencement (in early 1997) of the dual-phase vacuum extraction system in the grassed area (Figure 1), a previously unidentified secondary source under the roadway was recently discovered being drawn towards the grassed area. This necessitated an extension to the vacuum well installation to cover the roadway area.

This paper presents the experience gained from the site investigations and pilot testing, the design adopted for the remediation system and the initial results of remediation monitoring in the grassed area during the past year. It is hoped that the final results of the remediation programme including those from the roadway area will be available towards the end of 1998.

This project forms part of the Construction Industry Research and Information Association (CIRIA) project on case study demonstrations of remedial treatments for contaminated land.

SITE CHARACTERISTICS

The site is located in Essex and is around 3.5ha in area. Developed in 1952-53 from a greenfield site, it has since been used for the production of various electronic components.There is anecdotal evidence that up to the mid 1970s a range of waste degreasing solvents were disposed of in a pit dug in what is now the grassed southern part of the site, an area of about 20m by 40m. There is also evidence that waste

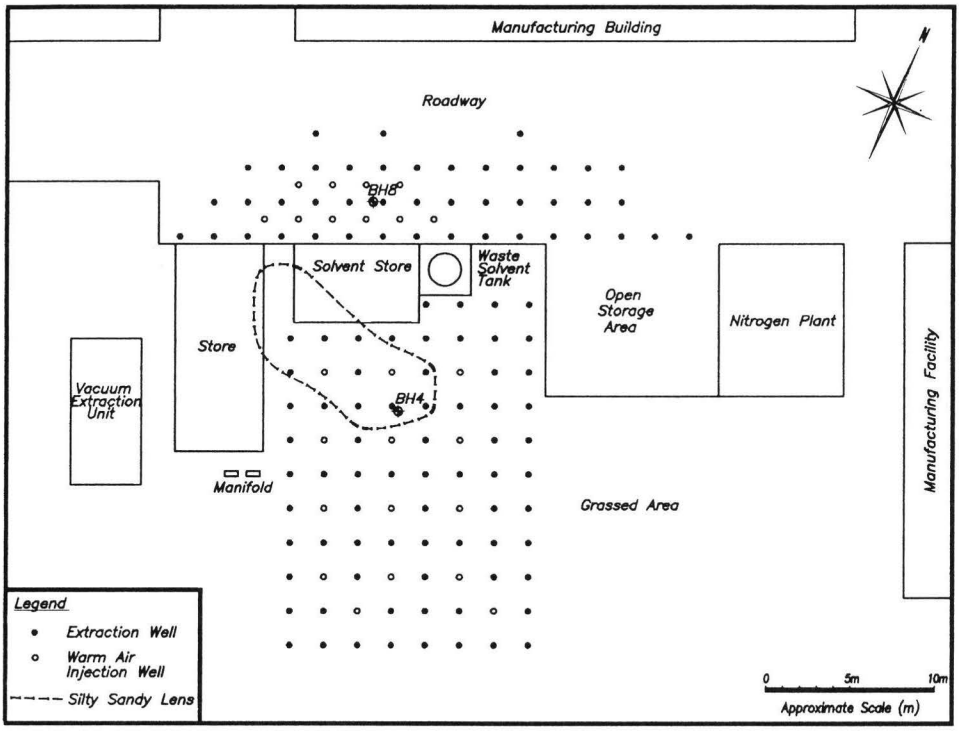

Figure1: Site Plan

automotive oils were also disposed of in this pit, believed to have been located near Borehole 4 (BH4) (Figure 1).

The range of contaminants in the grassed area includes volatile compounds (e.g. the chlorinated solvents trichloroethene (TCE) and 1,1,1-trichloroethane (TCA)) and semi-volatile compounds (e.g. PAHs and phthalates). The roadway area exhibits a similar mix of contaminants with the addition of vinyl chloride, a degradation product, as discussed later.

SITE GEOLOGY

The site geology is that of the London Basin consisting of the London Clay overlying the Lambeth Group, Thanet Sands and the Chalk. Quaternary glacial deposits cover the area of the site. The Chalk, a major aquifer, is at a depth of 30 to 35m. The beds of the Thanet sands and Lambeth group are mainly fine to medium sands but with some clay layers and they are thought to be 10 to 15m thick at the site location. The London Clay is about 15m thick and is encountered at about 12m below ground level. The glacial drift comprises brown and grey silty clays containing chalk clasts and flints (glacial tills). Poorly sorted sand and gravel horizons are present in the tills. These are of unknown lateral extent.

SITE INVESTIGATIONS

The grassed site area has been the subject of three site investigations undertaken by different parties and including trial pitting, boreholes and standpipe installation and, more recently, static cone penetrometer testing coupled with the Laser Induced Fluorescence (LIF) technique. Additional information on the near-surface stratigraphy of the site was obtained during the installation of the closely spaced vapour extraction wells.

The results indicate that the major part of the soil contamination in the grassed area occurs in a valley shaped glacial silty sand deposit flanked and underlain by glacial clay till, see Figure 1.

The silty sand layer below the grassed area and under the western end of the roadway area is approximately 13m long and 5m wide, running in south-east to north-west direction. The maximum depth recorded to the base of the layer is around 5m below the ground surface, with steep interfaces against flanking clay strata. *In-situ* water permeability tests indicate a hydraulic conductivity of 10^{-6} to 10^{-7}m sec^{-1}.

The results from the site investigation carried out at the junction of the grassed area and roadway areas did not indicate any significant contamination of either the soil or groundwater. Based on this information and anecdotal evidence regarding the disposal site, the initial vacuum well installation carried out in December 1996 covered the grassed area only. After several months of vacuum extraction, it became evident that a secondary source of contamination is present under the roadway area.

The glacial clay was found to comprise predominantly stiff grey or brown, sometimes mottled silty clay with much chalk, flint and other gravel, typical of a glacial till. Within this grey brown clay were found occasional thin (less than 100 mm) layers of clayey silt with some chalk gravel. The clay size fraction (less than 2 microns) varied from 33 to 46% and the laboratory measured hydraulic conductivity was in the range 1.3×10^{-10} to 2.4×10^{-11} m sec^{-1}.

SITE HYDROLOGY

The variation in groundwater level monitored in the piezometers is mainly a function of the depth at which the piezometer screens were installed. The groundwater levels are generally lower in the deeper screens. This reflects the historical water abstraction from the chalk aquifer, where published hydrogeological information[3] indicates a piezometric level some 25m below the ground surface, in the chalk.

The downward hydraulic gradient in the till makes it difficult to determine any overall horizontal direction for the groundwater flow, although the groundwater levels in the underlying sands and gravels seem to indicate flow in the southerly or south-easterly direction.

VAPOUR, SOIL AND GROUNDWATER CONTAMINATION

A soil vapour survey was carried out in 1995 in the grassed area in order to determine whether any significant concentrations of VOCs could be identified within the shallow unsaturated zone beneath the grassed area.

A series of vapour sampling points at approximately 1m depth were installed on a 5m grid across the grassed area. Peak VOC vapour concentrations of 181ppm were measured near the reported disposal pit in the vicinity of Borehole 4.

Following the soil vapour survey, 18 static cone penetrometer tests (CPT) were carried out across the grassed area using an 18-tonne truck-mounted CPT rig. The CPT locations were largely along north-south and west-east sections through the centre of the area of known contamination to provide continuous profiles of the geology and contamination.

The CPT rig was also equipped with a LIF cone in addition to the standard friction cone. The LIF cone directs a laser beam into the soil and measures the fluorescence induced by the presence of certain hydrocarbons, allowing continuous profiling of these compounds. Because the LIF does not induce fluorescence directly in the solvent compounds, the use of the LIF device was dependent upon the compounds found being associated with the solvents, namely petroleum hydrocarbons and semi-volatile organic compounds. The CPT rig was also used to obtain relatively undisturbed soil samples and for the installation of standpipes in some of the probe locations. The latter operation was not successful because of the lack of a sand filter around to the piezometer tips.

The results of the CPT/LIF investigation supported by evidence gained during the well installation indicated that the contamination in the grassed area occurred in an approximately 1.5m thick silty sand layer at a depth of approximately 4-5m below the ground surface. However, in places relatively low level contamination was detected to a depth of about 8m.

The water levels in the silty sand layer were typically 2-4m below the ground surface. For screens at 10m depth, the piezometric level was typically 5m below the ground surface.

In the roadway area, the information gained during installation of the wells indicated that the zone of soil and groundwater contamination extent is as shown in the well layout (Figure 1). The depth of the contamination extends to around 8m depth with the greatest concentrations in the 0-3m depth zone. The groundwater levels in the roadway area are currently 4-5m below the ground surface, although depressed to 6-7m near the actively treated wells in the grassed area.

The contamination in the grassed and roadway areas includes free product, dissolved phase and vapour phase in the vadose zone. The results from sampling soil, free product, water and vapour indicate the presence of several distinct groups of volatile

and semi-volatile contaminants. The volatile contaminants include chlorinated solvents, ketones and aromatic hydrocarbons (BTEX) compounds. The principal components are the chlorinated solvents TCA, CCl_4, TCE and Freon 113, these accounting for 80% of the mass of the free product. Semi-volatiles are also present at significant concentrations and include TPH, pthalates and PAHs.

The results of the soil chemical analyses indicated the presence of volatile organic compounds in significant concentrations in some of the soil samples, including acetone, DCM, TCA, TCE, PCA, Freon 113, xylene, toluene, and ethylbenzene. Their presence would appear to reflect the composition of the free product DNAPL. The TCA and TCE concentrations detected were particularly high, up to 6,000 and 4,235 $mgkg^{-1}$ respectively. TPH compounds were detected up to $111mgkg^{-1}$. Semi-volatiles were largely absent or at relatively low concentrations for the samples tested. The substances detected included a number of PAHs (naphthalene and 2 - methylnaphthalene), and phthalates (di-n-butylphthalates and bis (2-ethlhexyl phthalate).

Around the area of contamination below the roadway, but particularly towards the east, a halo of vinyl chloride was detected at concentrations of up to $2700\mu gl^{-1}$ in groundwater. This more toxic degradation product of TCE is likely to have resulted from the anaerobic degradation of TCE under the roadway[4].

Samples of groundwater from the area investigated have been taken over a number of years. Of three boreholes in the immediate vicinity of the known area of contamination, only one borehole, BH4 (which contained free product DNAPL) indicated significant dissolved-phase contamination of the groundwater. The concentrations of VOCs in this borehole are at or above their solubility limits. The TPH concentration measured was up to $180mgl^{-1}$ which exceeded its water solubility and suggests that the high concentration of chlorinated solvents may be acting as a co-solvent to increase the water solubility of the TPH compounds. The distribution of semi-VOCs mirrors that of the VOCs, as a number of semi-VOCs were detected at significant concentrations, most notably dimethyl phthalates at 10,000 $\mu g1^{-1}$ compared to the Dutch Intervention level of 5 $\mu g1^{-1}$.

CONTAMINATION RISKS

The hazards in the grassed and roadway areas of the site relate to the presence of volatile, semi-volatile and TPH compounds.

It appears that disposal of these products consisted of dumping the waste materials into a pit excavated for this purpose. As a result -and because of the generally low permeability of the soil strata- the soil vapour survey carried out in the grassed area indicated elevated vapour concentrations around the area of disposal (in the vicinity of Borehole 4). Surface air measurements were below detection limits. Also, the grass cover showed no sign of distress. It was considered that the risk associated with inhalation by humans of contaminated vapour in and around the grass area was small. A much more significant risk of vapour inhalation would apply to any future excavation

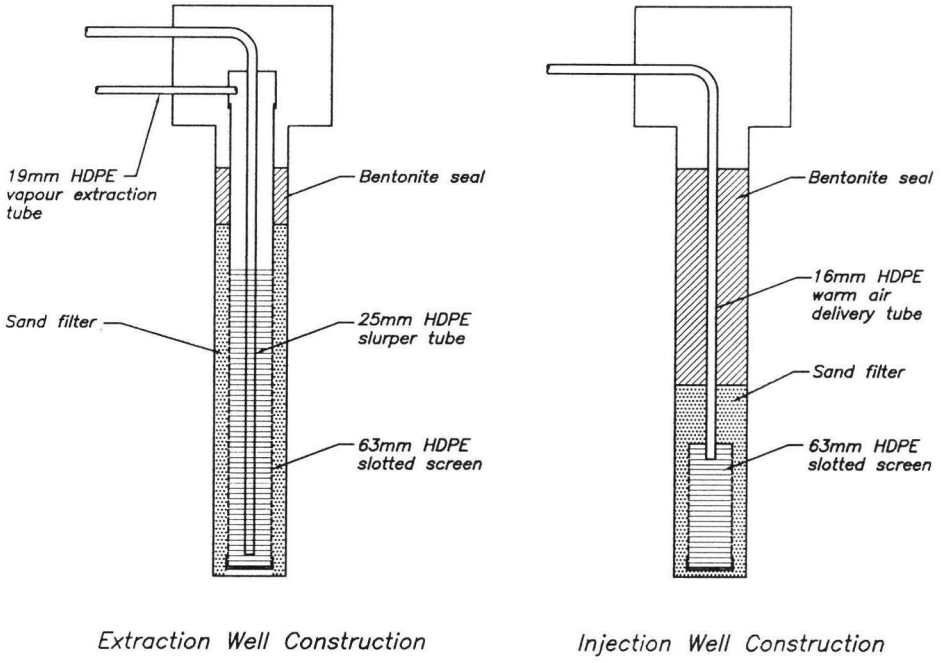

Figure 2: Well Construction

activities at the site, in connection with the installation of services, excavations for future development, and the like.

There was no evidence of significant off-site migration of contaminated groundwater. However, since the site lies approximately 1km south of a river, the possibility of groundwater contamination reaching the river was assessed. The conclusion reached was that dilution of the groundwater along its flow path to the river, coupled with dilution in the river, makes this risk relatively low.

Similarly, the risk of contamination of the chalk aquifer underlying the site was considered to be low, because of the thickness of the low permeability London and Lambeth Group Clays.

The main risk associated with the site relates to possible excavations in the grassed area. The residual, though very low, risk of off-site migration of groundwater contamination to the river is kept under constant review.

REMEDIAL OPTIONS

Two remediation options were considered for the site, namely, excavation and disposal of the contaminated soil and groundwater and an *in-situ* dual-phase vacuum extraction system.

The relatively small area affected by the contaminants would have made the excavation and disposal option attractive. However, there were three severe constraints against this option.

The first was the need to support the structure of the manufacturing building along the northern boundary of the roadway area.

The second was the presence of a manufacturing facility approximately 25m to the east of the grassed area in which there is a process which is extremely sensitive to vibrations. Thus any construction activity involving excavation support (e.g. sheetpiling) could have posed a significant risk to the facility. Indeed, for the vapour well installation the specification required the use of an auger drill rig rather than the more common percussion boring to reduce vibrations at the site. In addition, vibration monitoring was carried out prior to (for assessment of background levels) and during the auger drilling to check that there were no adverse effects on the manufacturing facility.

The third constraint was the sand and gravel glacial layer, underlying the glacial till which would have either had to be cut off by the installation of a deep and expensive cut-off trench wall into the London Clay, or dewatered to prevent heave of the base of the excavation. The dewatering option would probably have required the disposal of large quantities of contaminated water.

The dual-phase vacuum extraction system was favoured for practical and economic reasons. Nevertheless, two possible problems were identified with this technique and solutions were put in place to overcome them. The first was the presence of low volatility phthalates among the contaminants. It was thought that the phthalates and other semi-volatile compounds which were held in solution in the more volatile chlorinated solvents might be released to the soil and groundwater, once the VOCs were stripped and removed from the ground. To overcome this potential problem, warm-air injection wells were incorporated in the scheme to enhance the recovery of these semi-volatile compounds and also to boost the micro-organism activity in the ground that would break down and degrade these semi-volatile compounds.

The second possible problem was whether the low permeability of the glacial till material would hinder the method's ability to draw the contaminants into the extraction wells. To overcome this, the wells were installed at a very close grid spacing of 2m, compared with the more usual spacing of 4-7m. For the relatively small area treated, the additional cost associated with the increased number of wells was small in relation to the overall cost of the remediation programme.

Discussions with the Environment Agency prior to commencement of the remediation programme indicated their preference for the *in-situ* treatment rather than the 'dig and dump' method; the latter being perceived by the Client as transferring the contamination problem from one location (the source area) to another location (landfill site), a view with which the Agency and Consultant concurred.

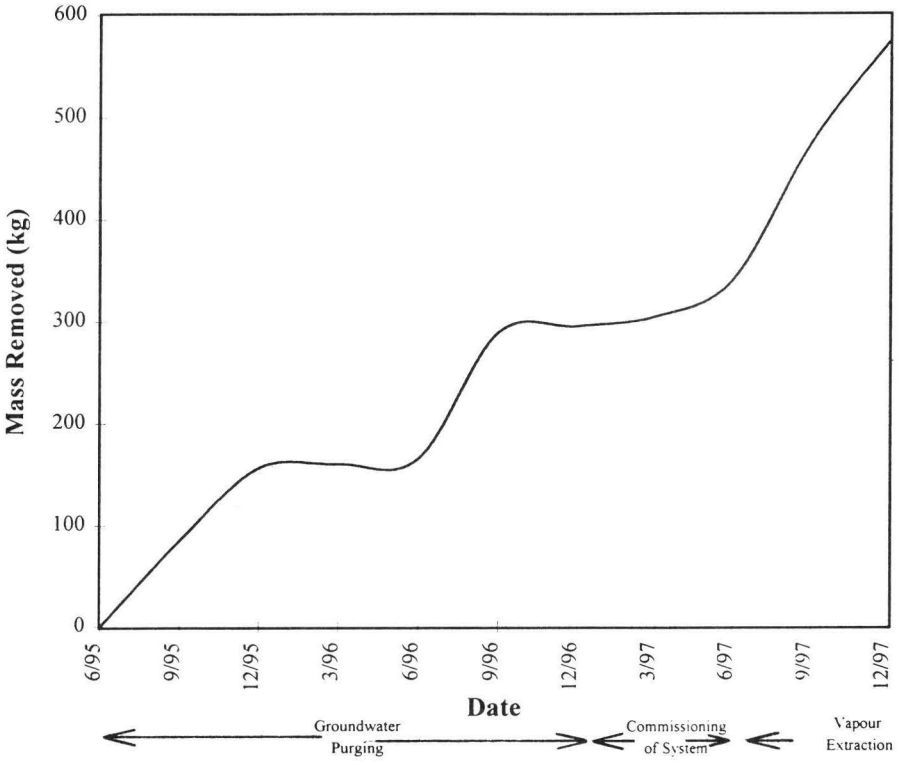

Figure 3: Cumulative Mass Removal of Contaminants

DUAL VACUUM EXTRACTION TECHNOLOGY CHARACTERISTICS

The basic *in-situ* vapour extraction system couples vapour extraction wells with blowers or vacuum pumps to remove contaminant vapours from zones permeable to vapour flow, thereby enhancing the volatilisation and removal of contaminants from the subsurface for treatment, as appropriate[2].

Where the groundwater table is relatively shallow, dual-phase vacuum extraction including the removal of liquids from the base of the well (slurping) can be employed to draw down the groundwater table while enabling vapour flow through the contaminated section of the ground (Figure 2)[5].

The treatment unit allowed for: (1) the collection of any free product for disposal to a licensed incinerator; (2) air sparging and activated carbon treatment of contaminated groundwater before discharge to the site sewer (or tankering to a licensed landfill site); and (3) activated carbon treatment of the combined air streams from the air sparging unit and vacuum wells before discharge to the atmosphere.

As part of the design process for the vacuum extraction system a pilot test was performed on an extraction well and three nearby monitoring wells. The results were

encouraging but the final design of the remediation system was based on the combined experience of the consultant and the remedial contractor MEL (including their Dutch associated company Recycling Nederlands) to finalise the design details for the remediation system required.

REMEDIATION PROGRESS IN THE GRASSED AREA

During 1995 and 1996 and prior to the commissioning of the vacuum extraction system, free product and contaminated water were removed by bailing and pumping from Borehole 4 and the other nearby observation wells. The total mass removed at the end of 1996 was around 300kg (Figure 3). Following commissioning of the extraction system in the spring of 1997, contaminated water and vapour accounted for a further 270kg of contaminated mass material. Virtually no free product was recovered, the reasons for which are not clear. It may be that bailing had removed most of the free product and that the remaining volumes are small and not easily detectable in the treatment unit, once the more volatile components have volatilised in the vapour stream.

It is interesting to note that an initial estimate for the mass of contaminants in the grassed area at the design stage was in the region of 10,000 to 20,000 kg, based on the volume of the silty sand layer affected by contamination, its porosity, etc. As the remediation programme progressed this estimate was continuously reduced to a current figure of around 1,000kg, which does not include the contaminants in the roadway area. This illustrates the uncertainty when estimating the mass of contaminants at the investigation stage.

The vacuum wells were operated in batches of 18 wells at a time to maintain a minimum sufficient vacuum (around 0.6 of an atmosphere). The measured air flow rate for each well group is about $30m^3h^{-1}$. Due to the low water permeability of the ground, the volume of contaminated water removed from each well group once steady state conditions are achieved is less than $5m^3$ per week.

Initially, the contaminated water was air stripped and then passed through activated carbon containers in order to meet the discharge limit conditions set by Thames Water. However, after several trials it soon became evident that the treated water met all the discharge consent limits except for TCA where the concentration after activated carbon treatment was around $18\mu gl^{-1}$ compared to the $10\mu gl^{-1}$ limit specified in the discharge consent. Fortunately, the volume of contaminated water removed is small and this allowed disposal to a licensed landfill site without prior air stripping treatment. Nevertheless, discussions with Thames Water are in progress to review the licence conditions.

The vapour stream has been treated through a series of six drums of activated carbon to meet the local authority health and safety discharge criteria of 1ppm for volatile compounds as equivalent to carbon tetrachloride.

For the majority of wells the concentrations of VOCs detected at the extraction manifold decreased markedly during the first 3 months (Figure 4). Vapour

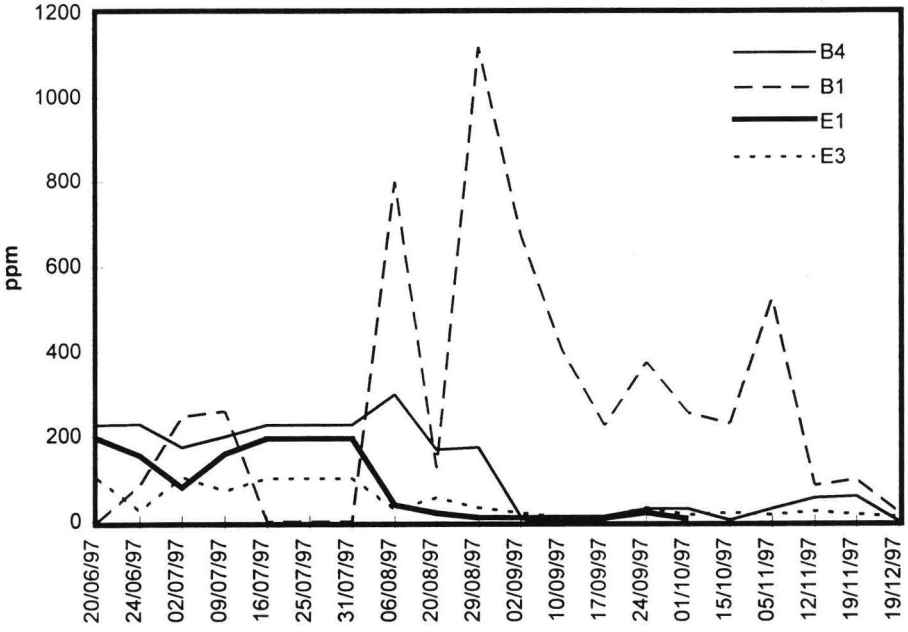

Figure 4: Total VOCs in Extraction Manifold

concentrations in a number of wells, particularly those close to the solvent store (e.g. B1, Figure 4) responded more erratically during the first few months of vacuum extraction. This may be the result of its proximity to the roadway area and also the extraction of contaminants through a number of different flow paths through the heterogeneous subsurface.

CONCLUSIONS

1. The innovative site investigation technique, Laser Induced Fluorescence (LIF), coupled with static cone testing provided valuable geological and contamination profiles in the grassed area.

2. The contaminants in the grassed area and roadway included free product volatiles and semi-volatiles in dissolved phase and vapour phase in the vadose zone.

3. The presence of nearby buildings, including a manufacturing facility extremely sensitive to vibrations, led to the adoption of an *in-situ* vacuum extraction technique instead of excavation and removal of contaminated soil and groundwater. The high clay content and low permeability of the soil necessitated a close well spacing of 2m and the installation of warm air injection wells.

4. Prior to the start of the vacuum extraction in Spring 1997 approximately 300kg of free product was removed by bailing and pumping from the existing observation wells. A further 270kg has been removed by the vacuum extraction system. The current

estimate of the mass of contaminants in the grassed area of 1000kg is very much less than originally thought.

5. The vacuum extraction system in the grassed area drew in a secondary contaminant plume from below the roadway. This plume had a vinyl chloride halo, likely to be the result of the anaerobic degradation of TCE under the roadway. Additional extraction wells have now been installed to cover the roadway area.

6. The remediation programme is on-going with final results expected to be available towards the end of 1998.

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REMEDIATION AND REDEVELOPMENT: A CASE STUDY

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Key Words: gasworks, groundwater treatment, in-situ remediation, PAH (polycylic aromatic hydrocarbons), remediation, risk assessment, soil washing, vacuum extraction, waste processing.

SUMMARY

A case study of the remediation works undertaken on the site of the National Millennium Experience site at Greenwich, London UK. The design of the remediation works was based on a series of very detailed investigations coupled with site specific environmental risk assessments which identified the significant contaminant sources, pathways and targets. Remediation works included the excavation and containment of a very deep tar well together with numerous shallower excavations and removal of smaller tanks. In addition, the installation of the largest soil vapour extraction system in the UK to date was undertaken together with the operation of a soils washing plant to minimise the quantity of materials for off-site disposal. Contaminated groundwater from the works was treated by an on-site treatment plant prior to disposal.

Contaminated Soil '98, Thomas Telford, London, 1998, 425–434

INTRODUCTION

This paper provides a summary of the remediation works which have been undertaken on the 300 acre Greenwich Peninsula site in London, UK which is to host the National Millennium Experience. The Greenwich Peninsula is strategically located immediately to the east of the Isle of Dogs, within the London Borough of Greenwich. The site is accessed from the A102(M) which emerges from the Blackwall Tunnel and runs along its western boundary.

GROUND CONDITIONS

Site Investigations

The ground conditions on the site have been determined through a series of increasingly detailed investigations which have been undertaken in a phased manner since the late 1980s. All of the investigation work has been carried out in full accordance with current best practice including that provided by British Standards, the DETR and the in-house guidance developed by British Gas.

In total some 2000 exploratory excavations and borings have been undertaken on the site and approximately 6000 samples of either soils or groundwater have been tested for a range of possible contaminants. All of the chemical analysis has been undertaken by accredited independent laboratories and has included the range of contaminants that may be present. Overall this represents a very detailed investigation of the ground conditions which in turn provides a high level of confidence in the evaluation of the contamination status and the development of appropriate remediation measures.

The ground investigation, has also been supplemented and influenced by the considerable amount of detailed information on the previous industrial use of the site..

Principal Contaminants

A large proportion of the overall Greenwich Peninsula site has been chemically contaminated to varying degrees as a result of former industrial activities, principally the generation of coal gas and associated by-products which were undertaken on the site for nearly 100 years. These included the manufacture of sulphuric acid and ammonium sulphate fertiliser in a dedicated chemical works as well as the production of coal tar and a range of organic chemicals, such as benzene and naphtha, in a separate tar works.

Due to the legacy of these processes the principal contaminants on the site comprised:

- wastes from tar production and distillation including coal tars and a variety of derivatives;

- materials from gas purification including spent oxide and foul lime waste;
- solid fuel residues including coal, coke and clinker.

Contamination Distribution

These principal contaminated materials were generally restricted to the made ground which comprised the upper 3-4m although, in a few instances usually associated with deep historical tanks, the contamination extended further into the underlying natural ground. The distribution of contaminants varied across the site and generally was related to the localised pattern of industrial landuse. The most significant contamination was associated with those parts of the site which were formerly occupied by the main gasworks processes or were used as explicit waste disposal areas.

Groundwater and Surface Waters

The potential for the contamination of groundwater or surface waters presented one of the major sources of environmental liability. Groundwater was present within two aquifers beneath the Greenwich site, firstly a relatively shallow aquifer in the Thames Gravels (at about 7m below ground level) and a second much deeper aquifer within the Thanet Sands/Upper Chalk. Of these two aquifers, groundwater within the Thanet Sands/Upper Chalk was viewed by the Environment Agency (EA) as the more significant resource, although apart from some limited industrial abstraction this aquifer is not currently exploited in the site area. Nor was groundwater within the Thames Gravels used for abstraction within the Greenwich Peninsula.

Water quality data from the Thames Gravels aquifer have shown widespread evidence of gasworks-related contamination, centred on those areas of the site which contained the more heavily contaminated soils. Groundwater within the Thames Gravels was also in hydraulic continuity with surface water within the River Thames which formed the north eastern boundary to the site.

In terms of deeper groundwater within the Thanet Sands/Upper Chalk aquifer, the water quality related primarily to the degree of protection afforded by the overlying relatively low permeability deposits (i.e. the London Clay and Woolwich and Reading Beds). Monitoring of groundwater quality in the Upper Chalk aquifer beneath the Greenwich site has shown it to be of good quality with no significant evidence of gasworks related contamination

Environmental Risk Assessment

The results of the investigations were used to undertake assessments of the level of environmental risk associated with the site, the results of which helped to define the required scope of the remediation works. The risk assessment processes used the

established methodology of identifying contamination sources, potentially sensitive targets (e.g. groundwater or people) and the pathways between these two. The most significant pollution linkages were thus defined. The scope of the designed remediation works then addressed these pathways by either partial or full removal of the hazard sources, (which has been the main method employed), or by modifying the pathways to specific targets e.g. by the installation of barrier layers or membranes.

Implications

The potential implications of the contaminated ground conditions can be split into four principal categories of receptors:

- surrounding environment, primarily soils, groundwater and surface waters;
- site construction workers;
- site users;
- building/infrastructure durability.

Of these the first category has been addressed by the statutory remediation works undertaken by British Gas Properties as the original polluter of the site. The remainder are being addressed by the development related remediation, which was the responsibility of English Partnerships.

OVERALL REMEDIATION STRATEGY

Introduction

The treatment of contaminated land is a necessary pre-condition for redevelopment of the whole Greenwich Peninsula, including the Millennium Experience site. Despite the presence of contaminated land on a large part of the site, there is no question that the development can proceed in an environmentally safe manner if suitable rehabilitation and protection measures are undertaken. The proposed rehabilitation strategy has been designed as the most appropriate in environmental, practical, and economic terms.

Remediation Concepts

The remediation works have been undertaken in two phases. An initial stage undertaken by British Gas addressed the main environmental risks which related mainly to the potential for long-term water pollution (termed statutory remediation). This was followed by additional remedial works which focused specifically on making

the site suitable for its intended uses. In essence, the remediation strategy has consisted of:

Statutory Remediation by British Gas

- removal or treatment of the contamination considered to represent the most significant long-term sources of pollution;

- **Development Remediation by English Partnerships**

- a flexible remediation approach depending on the nature and extent of the residual contamination (i.e. following completion of the British Gas remediation works) having due regard to the proposed end uses;

- leaving some contaminated materials in place, subject to the approval of the regulatory authorities, and isolating them from site users and other environmental receptors through, for example, construction of physical barriers;

- measures to prevent the accumulation of methane and other gases, as necessary;

- measures to prevent the movement of residual contaminants to clean areas through the construction of vertical barriers;

- strict quality control monitoring of the measures taken;

- keeping of comprehensive records to ensure that any future site excavation or redevelopment should not unknowingly disturb remaining contaminants.

The design philosophy adopted provided a cost-effective remedial solution which both minimised the longer term environmental risks and provided a safe completed development in terms of the eventual users of the site. Complete removal and/or treatment of all contamination within the site was considered to be inconsistent with Government policy and inappropriate in terms of both practicability and cost effectiveness. The estimated cost of such an exercise was considered to be prohibitive and inconsistent with the additional marginal benefits that would be gained, in terms of the further reduction in the residual contamination risks.

STATUTORY REMEDIATION WORKS

Statutory Remediation Strategy

The strategy for the statutory remediation works was developed by means of site specific risk assessments which took into account the statutory regime for contaminated land to be introduced by s57 of the Environment Act 1995 and currently detailed in Draft Statutory Guidance. The principal objective of the statutory remediation works undertaken by British Gas Properties was to address, by appropriate and cost effective means, selected contamination zones which, given the current status of the site and independent of site redevelopment, were likely to be the cause of either (i) significant harm or (ii) pollution of controlled waters (surface and groundwaters). These two criteria reflected the statutory definitions of 'contaminated land'.

The main potential environmental receptors were considered to be controlled waters, primarily groundwater in the Thames Gravels and the River Thames. Hence the main emphasis of the statutory remediation works was to minimise long-term risks to the water environment.

The outcomes of the risk assessments was the identification and remediation of the major contamination sources which are deemed to present a significant risk when compared with the criteria outlined above. The use of concentration-based remediation criteria was explicitly and deliberately avoided in determining the remediation strategy. Hence the approach was based on demonstrating that the overall mass of the significant contamination on the site has been reduced to an acceptable level as judged collectively by WS Atkins, the Environment Agency and the Environmental Health Department of the London Borough of Greenwich.

On completion of the statutory remediation works undertaken by British Gas Properties some residual contamination remained which was deemed, in the absence of any development, not to represent a likely cause of either significant harm or water pollution. To identify, and then remediate, these very localised 'hotspots' would, as discussed above, effectively require the whole of the made ground across the site to be excavated and sorted. It was agreed with both the Environment Agency and the Environmental Health Department of the London Borough of Greenwich that this approach would inappropriate in terms of cost-benefit and would also be inconsistent with the Government's policy on the remediation of contaminated land.

Scope of Statutory Remediation Works

The scope of the statutory remediation works concentrated principally on the removal of the major contamination sources which were considered to be the potential cause of significant harm or water pollution. The works involved the following:

- removal of the contents, structure and residues from the main tar well on the north of the site together with the removal of a large number of other smaller below ground tanks and wells;

- excavation and selective off-site disposal of major contamination sources to licensed landfills;

- physical treatment of selective excavated materials i.e. screening and washing to reclaim the reusable fraction for backfill to excavations;

- insitu remediation of volatile hydrocarbons, such as benzene, using a dual phase groundwater and soil vapour extraction system over an area of approximately 4.5 ha;

- extraction and on-site treatment of contaminated groundwater from all excavations and the area subject to in-situ treatment, prior to discharge to foul sewer.

Whilst considerable quantities of contaminated soils were taken off-site to licensed landfills, every effort was made during the course of the works to keep the quantity to a minimum through the use of innovative remediation technologies such as soil washing and soil vapour extraction.

Validation

During the course of the works, a programme of validation testing was undertaken the results of which were submitted to both the Environment Agency and the Environmental Health Department of the London Borough of Greenwich. This information also detailed the extent of the remaining contamination which fell outside the scope of the statutory remediation works. On the basis of the validation results it was concluded that all of the significant pollutant linkages identified in the risk assessment process had, within practical limits, been addressed by either removal of the source or modification of the pathway. Both Environment Agency and London Borough of Greenwich staff undertook periodic site inspections during the course of the works and regular audit reports were submitted by the Resident Engineer.

DEVELOPMENT REMEDIATION

Introduction

The residual contamination was addressed by English Partnerships through a package of additional measures in order to facilitate the further development of the site for specific end uses.

The significance of the implications associated with the residual contamination depended on the form and sensitivity of the proposed development. As outlined earlier, the accepted approach within the UK is that contaminated sites should be remediated to a standard which is 'suitable for use'. Hence the implications of the residual contamination will be more significant for uses such as residential development with gardens than for commercial uses which comprise principally 'hard' cover and which do not permit the same potential for human interaction with the ground.

The scope of the English Partnerships development remediation works related specifically only to the known end uses. For instance the land to be used as the Millennium Experience coach park was remediated only to make it suitable for that explicit purpose. When the future long term use is agreed and implemented, after the completion of the Millennium Experience, further remediation works are likely to be required to suit the new proposals.

Remediation Strategy

The principal objective of these secondary, development-related remedial measures was to ensure that the ground conditions were appropriate for the intended end use.

The other main objectives of the development remediation strategy were to mitigate the potential impacts on the construction work force, and building fabric of the proposed scheme in addition to ensuring that any further adverse implications for the surrounding environment were minimised.

The design of these remediation works also taken due account of the anticipated duration of various components of the scheme. Hence a distinction was made between those components which were intended to have only a short term use and any permanent legacy features. This issue of distinguishing between relatively short term uses for the Exhibition and long term development uses, in terms of the extent of remediation measures, was discussed and agreed with both the Environment Agency and the Environmental Health Department of the London Borough of Greenwich.

Site Users

Barrier Systems

The dominant development remediation technique used on the site was the isolation of contaminants from the site surface through the construction of a barrier layer system. This system comprised a sandwich construction of different materials which prevented both migration of, and human contact with, the contaminated ground. A vital part of this sandwich was a capillary break layer, comprising coarse granular

material (e.g. graded crushed concrete), which prevented upward movement of soluble contaminants into the clean zone via the process of capillary rise.

A further important component of the barrier system was a brightly coloured plastic mesh 'marker layer' which was laid on the upper surface of the residual contaminated ground and which provided a clearly visible indicator in the event of future disturbance, for example during future maintenance works.

Above the break layer was a layer of relatively low permeability soil, clay for example, which acted as an additional protective layer. The thickness and quality of this soil layer was dependent on the ground conditions in a particular area, the proposed form of end-use and the proposed final ground levels. The total thickness of the barrier layer typically varied from 0.5m to 1.0m.

In landscaped areas, clean soils were imported to a depth consistent with the required form of planting. The barrier system was designed to be appropriate for the underlying degree of contamination and the soil thickness needed for planting. In general, extensive barrier systems were not required beneath 'hard' forms of development such as buildings and roads. In these cases conventional construction was designed to provide the necessary protection, in terms of physical separation, for users of the site from any residual contamination

Barrier systems, together with the completed development, also reduced permeation of rainfall into the residual contaminated ground, so reducing any future leaching into groundwater. Within the permanent Central Park area the capping layer conformed to the current requirements of landfill design and as such effectively prevents the entry of water into the underlying ground.

The remediation design also included measures to minimise possible migration of residual contamination between untreated and treated areas. In particular measures were incorporated into below-ground services corridors which traversed contaminated areas to ensure that they could not act as transmission routes for the movement of contaminated groundwater.

Gas and Vapour Controls

The principal residual contamination issue to be addressed in relation to the Dome is the presence of volatile hydrocarbons within the underlying made ground. The main compounds of concern were benzene, and other odorous organics including oils, creosols, phenols and tars. Additionally there was a very low risk associated with methane derived from the peat horizon which underlies the site.

The level of risk associated with benzene has been evaluated by means of a quantified assessment and has been shown to be acceptably low even in the absence of any

specific control measures. However, the incorporation of gas control measures into the floor of the Dome is considered to be a reasonable precautionary step to ensure that an already very low risk is further minimised as far as practical.

The protection measures proposed have involved a low permeability barrier membrane which provided a substantial permeability differential with the underlying made ground and any sub-base material.

Surface Water Protection

As part of the development works measures were incorporated, such as bentonite/cement slurry walls, to ensure that any remaining perched water could not impact either the development itself or the River Thames. In particular, measures were incorporated in those areas where the usual river wall design was modified to create environmental features and there was an increased potential, in the absence of such measures, for perched water to enter the river.

Keeping Records

The final ground conditions, including the nature and extent of remedial measures adopted, are being fully recorded so that this information can be made available by English Partnerships in the longer term for any subsequent works or development on the site. It is likely that data will also be stored by the local authority, although the final details of such a record system are still to be decided. In addition the Health and Safety File for each area of the site will be made available to future purchasers under the CDM Regulations.

Acknowledgements
The author gratefully acknowledges the assistance received from both BG plc Property Division and English Partnerships.

IN-SITU BIOREMEDIATION OF CHLORINATED HYDROCARBONS IN GROUNDWATER

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Key words: In-situ bioremediation, chlorinated hydrocarbons, aromatic hydrocarbons, microbiological degradation, groundwater remediation, groundwater sampling, sampling techniques

ABSTRACT

Contamination of groundwater with aromatic, aliphatic and chlorinated hydrocarbons can be successfully remediated by in-situ bioremediation. To optimize the biological degradation of pollutants, different redox conditions (methanogenic / methylotrophic) have to be generated in the aquifer. A case study is presented to illustrate the different steps of treatment and the observed reactions.

KURZFASSUNG

Grundwasserverunreinigungen mit aromatischen, aliphatischen und chlorierten Kohlenwasserstoffen können mittels einer biologischen In-situ-Sanierung erfolgreich beseitigt werden. Um einen optimalen Schadstoffabbau zu erreichen, müssen im Grundwasserleiter verschiedene Redoxbedingungen (methanogen / methylotroph) erzeugt werden. Anhand einer Fallstudie werden die verschiedenen Teilschritte und die beobachteten Vorgänge dargestellt.

RÉSUMÉ

Il est possible de remédier des aquifers pollués avec des hydrocarbons aromatiques, aliphatiques et chlorinés avec une méthode de remédiation biologique in situ. Pour achever la dégradation complète des polluants, des milieus rédox différents (methanogène / methylotrophe) doivent être produits dans l'aquifer. A base d'un cas exemplaire, les différents étapes de la procédure et les réactions observées sont présentés.

Contaminated Soil '98, Thomas Telford, London, 1998, 435–443

INTRODUCTION

On a former chemical factory site near Heidelberg/Germany extensive soil and groundwater contamination was detected in 1982. Various chemicals had been used over a period of more than 30 years and had contaminated the soil at production facilities, storage areas and near the sewage system. Chlorinated, aromatic and aliphatic hydrocarbons were the main contaminants, with concentrations up to 80,000 µg/l CHC, 860 µg/l BTEX and 500,000 µg/l aliphatic hydrocarbons. A plume of several hundred meters in length had formed in the sandy, permeable aquifer. It was highly likely that contaminants would migrate to the waterworks downgradient from the site. Before the start-up of the biological remediation, groundwater had been pumped from the wells over several years until 1989. After a fast initial reduction of pollutants, concentrations were stagnating at a level of several thousand microgramms per liter. It was obvious that unless changes to the remediation approach were introduced groundwater extraction and treatment would have to be continued for a long period of time.

BASIS OF REMEDIATION DESIGN

Before the start-up of remediation measures, size and location of the contaminated areas were investigated with the help of soil vapour sampling in a 10 m x 10 m grid. Main sources of contamination had been the former laboratory, the sewage system and a chemical storage site. 20 groundwater monitoring wells were installed on-site and downgradient in order to characterize the extent of groundwater contamination.

For the planning of the infiltration system and for the optimization of the nutrient dosage, it is important to be familiar with the vertical pollutant concentration profile in all parts of the aquifer. This is usually difficult to determine. A new groundwater sampling system was developped for the vertical profile investigation of contaminants in the aquifer. The IBL multilevel well systems consist of small filter screens and submersible pumps that are inserted into the borehole. Subsequently, the casing is slowly withdrawn from the borehole in a way that the natural stratification of the aquifer recovers around the compounds of the multilevel system. The IBL multilevel well (patented by IBL GmbH, Heidelberg, Germany) is a fast and cost-effective way to gather representative groundwater samples from high amounts of sampling depths. Five IBL multilevel wells with up to 10 sampling levels each were installed in depths of up to 40 m (which is the thickness of the aquifer).

The next step in the planning of the remediation was to evaluate the efficiency of the authochtonic microorganisms for degrading all contaminants present on-site. The

limiting factors for the degradation of non-chlorinated and chlorinated pollutants were defined in laboratory tests. Furthermore, different nutrients and cosubstrates were added to the groundwater samples to obtain information about the dosage rates that are necessary to optimize the microbial degradation process.

A field pilot study over 5 months showed that the contaminants could also be removed from groundwater under field conditions. During the field study, infiltration rates and the effectiveness of cosubstrates to induce anaerobic conditions in the aquifer were tested.

REMEDIATION PROCEDURE

Based on the encouraging results of the laboratory and field scale tests, the remediation system was designed and installed. The goal of the remediation design was to combine a "pump and treat" method necessary to prevent further migration of contamination, with microbial decay stimulation. Groundwater (up to 15 m^3/h) was extracted from six remediation wells and treated using UV oxidation and a stripping plant. 5 m^3/h were enriched with nutrients, oxygen or cosubstrates and infiltrated to the unsaturated and saturated zone via infiltration wells. Accumulated floating product in one of the wells was removed with an oil recovery system. The remediation system is shown in figure 1.

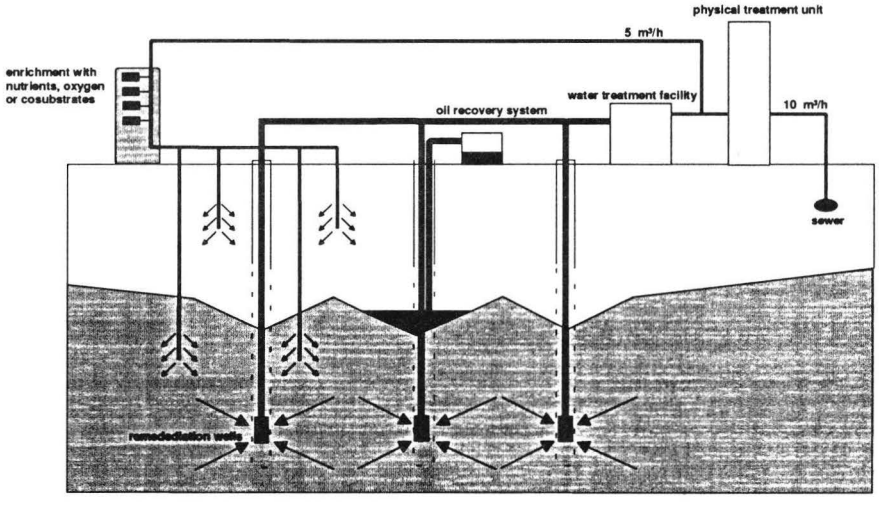

Figure 1: Procedure and hardware compounds of the in-situ bioremediation method

BIOLOGICAL TREATMENT

The different contaminants required different biological treatments. Aromatic and aliphatic hydrocarbons are used by microorganisms as source of carbon and energy under aerobic conditions, whereas chlorinated hydrocarbons are broken down preferably by cometabolic processes in anaerobic environments. The pathways of the microbial decay of chlorinated hydrocarbons were investigated by Vogel and McCarthy (1985). The challenge involved with this project was the realization of the required redox conditions and nutrient supply under field conditions. The most important properties of environmental systems, compared to laboratory systems, are the heterogenity of the aquifer (e.g. vertical anisotrophy) and the great amount of reaction compounds and processes that exist simultaneously. External influences (e.g. the presence of substances in the groundwater that take part in the reactions, like nitrate) and the higher amount of concurring processes make it more difficult to realize the desired reactions. Moreover, clear cause-effect-relationships between the parameters involved with the reactions cannot always been observed.

The microbiological remediation consisted of three steps. At the beginning of the treatment, nutrients and oxygen were supplied to enhance and accelerate the degradation of non-chlorinated compounds. Nutrient content and microbial activity in the aquifer were monitored continuously to calculate the required amount of substances.

After the removal of non-chlorinated compounds, anaerobic conditions were artificially created in the aquifer by supplying cosubstrates (substances with a high biological oxygen demand). The redox potential decreased quickly after the infiltration of these readily degradable substances. However, the optimum rates of reductive dechlorination can only be achieved under methanogenic conditions. At lower rates, degradation of CHC can also take place under sulfate-reducing conditions. The redox potential cannot reach the required values of less than -200 mV as long as nitrate as preferred electron acceptor is still present. Nitrate and oxygen concentrations in groundwater in the peripheral areas made it difficult to achieve methanogenic conditions throughout the aquifer. However, reductive dechlorination of CHC occured in subcompartments. After four years, the concentrations of the highly chlorinated CHC had decreased enough to start the third phase of the remediation.

Oxygen was supplied again to enable the microorganisms to fully degrade all metabolism products that possibly had accumulated under anaerobic conditions.
In the last year of the remediation metabolites were removed and the microflora was able to return to undisturbed, natural rates of growth and activity.

MONITORING OF REMEDIATION SUCCESS

The ongoing microbial processes were monitored through the sampling of the six remediation wells and other monitoring wells. Of particular importance was the information from the multilevel wells about pollutant and nutrient concentrations as well as the redox conditions in the different layers of the aquifer.

Figures 2 and 3 illustrate the course of the pollutant concentration in the remediation well B 106, located in the center of one of the contaminated areas. The vertical distribution profile of the various compounds in multilevel well 19, at a distance of 10 m to B 106, is shown in figures 4 to 7. In 1990, the annual medium concentration of CHC was as high as 4,500 µg/l in B 106 (figure 2) and in ML 19 at the highest level (at 6 m below ground at the top of the saturated zone). In B 106, aromatic hydrocarbons were present at concentrations of 500 µg/l (figure 3). The presence of aliphatic and aromatic hydrocarbons with a density < 1 g/cm³ had prevented the chlorinated hydrocarbons from sinking to the bottom of the aquifer.

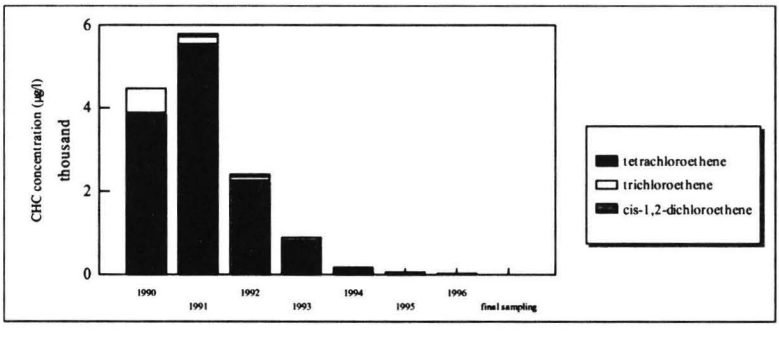

Figure 2: Medium annual concentrations of chlorinated hydrocarbons in remediation well B 106

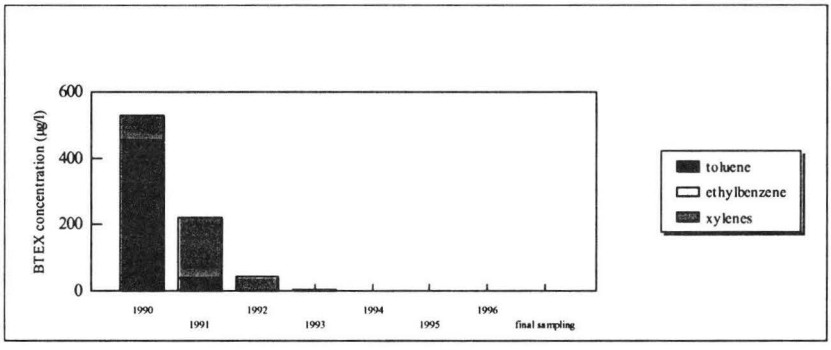

Figure 3: Medium annual concentrations of aromatic hydrocarbons in remediation well B 106

To remove non-chlorinated hydrocarbons, oxygen was supplied in the first phase of the treatment. In 1991, aromatic hydrocarbon concentrations had been reduced by half, whereas chlorinated hydrocarbons showed an increase (figures 2 and 3). This increased mobility of the pollutants is caused by the stimulation of microbial activity, which also manifested itself in a rapid increase of groundwater temperatures by 4-5°C in the first six months of treatment.

Further mobilization of pollutants lead to the accumulation of aromatic and aliphatic hydrocarbons as floating product with a thickness of up to 75 cm on top of the aquifer. In the second and third year of the treatment (1991-1992), more than 500 l of floating product were removed with a recovery system.

After the initial increase of CHC concentrations, a rapid decrease (> 50%) occured in the third year of the treatment (see figure 2). The high oxygen demand of the aerobic degradation processes of aromatic and aliphatic hydrocarbons had created anaerobic areas in the aquifer even though oxygen was continously supplied. The oxygen concentrations in B 106 were usually less than 3 mg/l during the aerobic phase. However, the analysis of groundwater sampled from the remediation well gives mean values that may as well represent very high and very low oxygen concentrations existing at the same time. In some levels of ML 19 anoxic conditions were often present during the aerobic treatment phase. In other subcompartments of the aquifer that were better supplied with oxygen, the aerobic degradation of non-chlorinated hydrocarbons and lower chlorinated metabolism products continued.

During the first part of the aerobic treatment, the fraction of tetrachlorethene increased as a consequence of the aerobic degradation of lower chlorinated compounds (trichloroethene and 1,1,1-trichloroethane). In 1991, more than 90% of the CHC

were tetrachloroethene (figure 4). Later, in the years 1992 and 1993, 1,2-cis-dichloroethene (product of the anaerobic cometabolism) appeared in considerable concentrations in the upper levels of ML 19 (figure 5).

Until 1994, aliphatic and aromatic hydrocarbons had completely disappeared. CHC concentrations had been reduced to about 200 µg/l. To achieve further and complete degradation of CHC, the anaerobic treatment phase was started. Cosubstrates were supplied via the infiltration wells. After the consumption of the available oxygen and nitrate, tetrachloroethene and trichloroethene were dechlorinated. The fraction of 1,2-cis-dichloroethene increased to approximately 90% of the total of CHC (figure 6).

After the CHC concentrations were below 30 µg/l and the metabolization to 1,2-cis-dichloroethene had been almost complete, no further improvements could be expected from the anaerobic treatment. The remediation was continued with the last aerobic phase. Metabolism products and cosubstrates, which had increased the dissolved organic carbon (DOC) content to up to 20 mg/l, were oxidized during the last year of the treatment. The oxygen content went up to 7 mg/l in B 106.

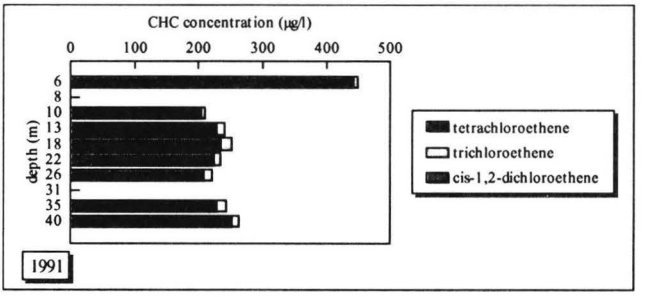

Figure 4: Concentrations of chlorinated hydrocarbons in multilevel well 19 - 1991

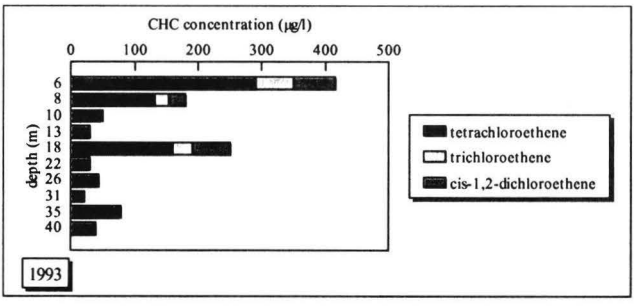

Figure 5: Concentrations of chlorinated hydrocarbons in multilevel well 19 - 1993

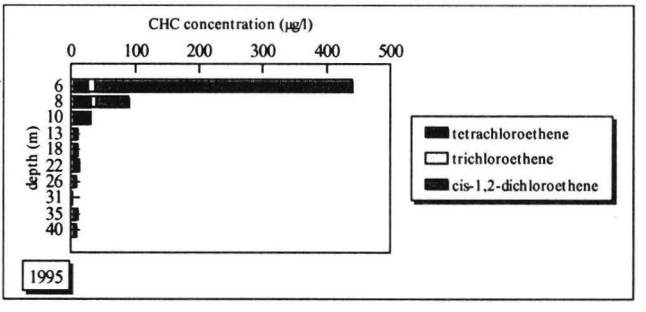

Figure 6: Concentrations of chlorinated hydrocarbons in multilevel well 19 - 1995

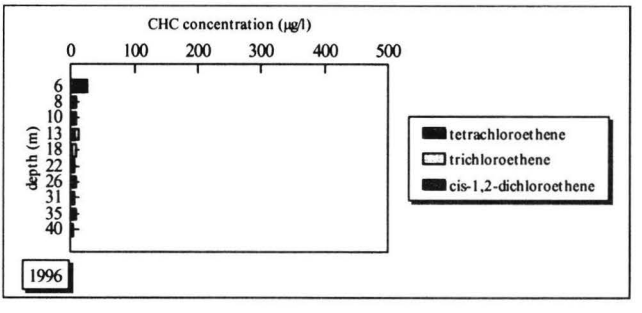

Figure 7: Concentrations of chlorinated hydrocarbons in multilevel well 19 - 1996

RESULTS

During the six-year operation period, all contaminants were reduced to levels below or near the detection limit. Sampling of soil, soil vapour and groundwater proved that the remediation had been successful. Groundwater contamination of CHC was about 10 µg/l in all remediation wells. In total, more than 24 tons of pollutants were removed from the site. In-situ aerobic and anaerobic biodegradation accounted for more than 90% of the remediation success.

It has been demonstrated that in-situ bioremediation of aquifers contaminated with chlorinated hydrocarbons is feasible within a time period that is short compared with the average time required for "pump and treat" methods. Biological degradation processes in-situ enhance the remediation progress twofold. Pollutants that are metabolized in-situ do not have to be removed by water treatment facilities, e.g. activated charcoal or stripping plants. Furthermore, they are effective even in subcompartments of the aquifer that are not reached by groundwater flowing through preferential pathways. As a consequence, the microbiological remediation is able to achieve low residue contamination levels and assures the long-term effectiveness of the measure.

ACKNOWLEDGEMENTS

The financial means for the remediation were provided by the Altlastenfonds Baden-Württemberg. We are indepted to Mr. Lutz Backhaus (Wasserrechtsamt Rhein-Nekkar-Kreis) and Dr. Wolfgang Kohler (Landesanstalt für Umwelt Baden-Württemberg) for valuable discussions.

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LARGE SCALE HEAVY METAL POLLUTION: THE CASE FOR AN INTEGRATED RISK AND LANDUSE MANAGEMENT APPROACH

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Key words: Authorities role, cadmium, case study, ecological effects, groundwater protection, human health risk, landfills, sustainable soil use, zinc.

SUMMARY

Soil and groundwater in the "Kempen" an area in the southern part of the Netherlands and the northern part of Belgium have been polluted by emissions of zinc smelters. The sheer size of the area and the combination of low level contamination with acidic sandy soils made the application of classical assessment and remediation procedures rather difficult. In large areas within the Kempen the pollution does not exceed the Dutch intervention values but important adverse effects can be shown to occur. Excavation and clean up is not possible for the whole area, the same holds for isolation control and monitoring approaches. Pollution affects "fitness for use" of the soil for agriculture, private gardening, and nature development. This will in turn restrict the possibilities for spatial planning. Leaching of top soils and sinters, the solid waste from zinc smelters which has been landfilled and reused all over the Kempen, will pollute groundwater, which is extensively used for drinking water and agricultural purposes. The Dutch Technical Soil Protection Committee recently reviewed the available information on the Kempen and recommends the development of a well coordinated management approach which integrates spatial planning, local risk reduction and monitoring of the pollution and it's effects.

Contaminated Soil '98, Thomas Telford, London, 1998, 445–452

INTRODUCTION

The Kempen, a large area in the southern part of the Netherlands and the northern part of Belgium has been polluted by zinc smelters. Similar situations can found elsewhere, for instance near the smelter at Avonmouth in the UK. Current contaminated land risk assessment and remediation approaches were not designed to cope with such large scale problems and do not lead to sustainable solutions. The Dutch Technical soil protection committee (TCB) recently recommended the development of an integrated risk and landuse management approach for the Kempen area (TCB 1997). Due to the persistence of metal contamination and the technical impossibility to remove all pollution a special permanent organization may be needed to coordinate land use planning, partial remediation, monitoring of the behaviour of the pollution and it's effects on human health, ecosystems and groundwater. The management approach has been accepted by the authorities which are now discussing the organizational aspects.

The present paper will highlight the basic issues of this integrated risk and landuse management. To put this approach in a proper perspective the extent of the pollution and the adverse effects that have been observed will be briefly described first.

CHARACTERIZATION OF THE POLLUTED AREA

The Dutch part of the Kempen contains the largest case of soil pollution in the Netherlands, around 150 km2. From 1892 to 1973 the zinc smelter near Budel used a thermal process to extract zinc from metal ore which caused the major part of the soil pollution in the Dutch part of the Kempen. Metals (mainly zinc, cadmium copper, lead) were emitted by the smelter to the air and through waste water. The waste water contaminated surface water and sediments and adjacent riverbanks due to flooding. The smelter also produced solid waste in the form of sinters which were landfilled or used as surfacing material for roads and farm yards. Metals leached from the sinters into the soil and may reach important aquifers. Due to acidification of the soil metal contamination will gradually leach into groundwater. Soil contamination will decrease and groundwater contamination will increase. Although concentrations of metals in topsoil in most areas are relatively low (below the Dutch intervention values) there is a very large amount of cadmium and zinc present in the soil that may lead to serious groundwater problems in future.

In 1973 the zinc extraction process was changed and emissions stopped. A new type of chemical is formed, which is stored in basins. One of these basins is now leaking. To prevent further contamination of soil and groundwater geohydrological isolation is applied to the site of the factory.

RISKS AND EFFECTS

Human health effects have been reported for the area by Kreis in 1987. Similar effects (on renal functions) have been observed in Belgium at higher levels of soil contamination (see for instance Staessen, 1994)

Accumulation of metals has been found in a number of soil invertebrates living in the organic layers of forest soils close to the smelter (Van Straalen and Van Wensem 1986). Genetic adaptation to the metals has been found for isopods at this location (Van Capelleveen 1987; Donker *et al.* 1993). Indications for genetic adaptation for springtails have been found by Posthuma (1992). These animals live in the organic layers of the soil. There are also indications for the disturbance of litter breakdown in forest soils close to the smelter, which results in litter accumulation (Oost and 't Hart 1994).

In the area around this zinc smelter, accumulation of metals has been found in vegetables from private gardens and commercially grown crops (Van Luit and Smilde 1983), in earthworms and moles from grass and heath lands (Ma 1987), and in the kidneys of cows (Spierenburg *et al.* 1988). There are indications for transport in metals through food chains (secondary poisoning) (Gorree *et al.* 1995).

Despite these serious effects on the soil ecology in the area around the smelter, the soil contamination is relatively low in level and small in area compared with other metal works, such as the smelting works at Avonmouth, UK (Hopkin *et al.* 1986) and the copper mill at Gusum, Sweden (Tyler 1984).

SOIL POLLUTION AT THE REGIONAL SCALE

Contaminated land clean up policies generally concern polluted sites, limited areas with heavy pollution, often with a single form of current or intended landuse. These sites mostly fall under the jurisdiction of a single authority for instance a municipality. Simple solutions like excavation and clean up or isolation are used as remedial measures. Remediation can be completed in a few years.

Pollution in the Kempen is occurring at a regional scale and is different in all respects. Heavy metal concentrations are rather low except in the close vicinity of the smelter and in the sinters in landfills, yet there are many adverse effects. There is much variation in landuse in the Kempen area and many changes in landuse can be foreseen, because the area is a focal point for new spatial planning and for nature development. Many authorities have to deal with the pollution in the Kempen: 2 provinces, 46 municipalities and a few water authorities. Classical clean up solutions are not feasible for the area as a whole, yet it has to

be treated as a single case of soil pollution according to the Dutch soil protection act.

Experience with remediation, isolation and control and risk management approaches for such large areas was not available in the Netherlands, and because there were no fast solutions available political attention for the pollution in the Kempen area decreased. Incidental partial excavation of sinters used as surface material and road construction material took place if a change in landuse was anticipated, and a number of private gardens were supplied with a clean top soil to prevent exposure to cadmium via consumption of homegrown vegetables. Treatment of all gardens in the Kempen would lead to enormous costs. It was then decided only to treat the gardens with the highest risk. A generic limit value of 2,5 mg Cadmium per kg. dry soil was proposed on the basis of research performed in the Kempen. Gardens with topsoil containing more than 2,5 mg/kg had to be treated.

The high costs associated with this proposal and the fact that other effects of the pollution than the risk associated with the consumption of home grown vegetables were likely to become more and more neglected were two reasons why the TCB was asked to make recommendations for a new approach the Kempen. Another reason was that "Active soil management", which started as a new policy concept to cope with persistent diffuse pollution in the larger cities in the Netherlands might provide a valuable model for a new approach in the Kempen.

The committee stated that an integrated risk and landuse management plan is needed to put all the negative consequences of the metal pollution in the Kempen in their proper perspective. Although much information is available on adverse effects of the soil pollution, the level of detail is often insufficient for local clean up decisions. For instance the aforementioned limit value of 2,5 mg Cd /kg soil is based on correlation between cadmium levels in vegetables and cadmium levels in soil. Although the correlation is significant there is an enormous variability. In fact a safe level cannot be established on the basis of these data. Because the consumption is an easily controlled risk factor a simple advice to be careful with the consumption of large quantities of homegrown vegetables unless their cadmium content can be proved to be safe (by taking some samples of the vegetables for instance) is more effective than replacing top soils above a certain value. Measures of this type are not acceptable as "clean up objectives" in a clean up policy but may be acceptable whithin a long term risk management framework .

Much of the research that was performed in the Kempen was primarily aimed at substantiating the claim that the pollution was serious in order to meet the criteria for funding of remediation on the basis of the soil protection act. Most of the time the research could not be used as a basis for specific remedial actions. Much research was also performed out of academic interest. The pollution provided an opportunity to study the consequences of soil pollution in the field. If the research could have been coordinated the contribution to a systematic picture of the state of affairs in the Kempen might have been larger. Scenarios of future developments of risks, adverse effects and groundwater pollution are badly needed to determine the optimal course of action for risk reduction and for land use planning in relation to limitations in landuse capability.

RISK AND LANDUSE MANAGEMENT

Due to the technical impossibility of classical clean up approaches and the extent of the polluted area, soil pollution will remain an important factor governing the social and economic development in the Kempen. Restrictions in landuse and in the use of groundwater must be known and must be studied and monitored, because they may change due to autonomous processes in soil and groundwater. To cope with these problems a structural management approach will be needed, which concerns the following aspects:

1]Knowledge of the geographical distribution and future behaviour of the pollution.

A map of the current soil pollution will not be sufficient. The leaching of the contamination may change the picture in future. Scenario studies for the prediction of future contamination must be performed. To evaluate the consequences of groundwater pollution the geohydrology of the area has to be studied in more detail.

2] The relation between soil and groundwater contamination and fitness for use.

Soil contamination may lead to the landuse restrictions. For a proper landuse management the relation between soil contamination and fitness for use must be known. Sometimes it is possible to reduce the restrictions by local cleanups, for instance the removal of sinters applied as surface material. Knowledge about simple measures that can be taken locally to improve landuse capability is very important and should be made available to the local authorities involved in landuse change decisions.

3]Monitoring of the adverse effects of the pollution

The development of natural ecosystems on the heavier polluted areas is slowed down. Yet some ecological recovery is occurring. It is important to monitor this development, not only for scientific purposes. Total cleanup op these nature

areas is too destructive but partial cleanups and control of autonomous changes may improve the situation. A learning by doing approach in nature development on contaminated land may be useful here.

In the past the concentration of cadmium in commercially produced vegetables incidentally exceeded the limit value for food. Monitoring of these products is important to answer the question whether limit values are still exceeded. The bioavailable fraction of the cadmium may be less than in the past due to leaching. A monitoring program is also useful to assess the performance of immobilization and phytoremediation approaches.

It maybe of interest to repeat the investigation of Kreis (1987) on human health effects. It might well be the case that after ten years due to the decrease in emissions to the air and the leaching of cadmium from the soil to deeper layers total exposure and health effects are decreasing. A decrease might promote the acceptance of the situation.

Monitoring of groundwater is important for predictions about the future consequences of groundwater pollution. Groundwater pollution is expected to increase due to leaching of topsoil and sinters that where applied throughout the Kempen. Groundwater monitoring is important at two spatial scales: a local scale to evaluate the quality of aquifers which are important for drinking water supply or for vulnerable terrestrial and aquatic ecosystems. A regional scale approach is needed to predict the spreading of polluted groundwater to other areas outside the Kempen.

4]Assessment of the effects of planned changes in land use on the behaviour of the soil contamination.
If one intends to change the use of the land it's fitness for the new use must be assessed. In addition the question whether the change itself will affect the pollution is also relevant. If the change involves excavation of soil or sinters one might use the opportunity to excavate some more to reduce landuse restrictions.

5]Changes in the environment that may influence the risks associated with the metal pollution must be taken into account.
Behaviour and bioavailability of heavy metals especially cadmium is strongly dependent on soil organic matter content and soil pH. Monitoring of acidification, changes in groundwater table and measures taken to solve other environmental problems (like the intensive animal manure problem) are needed to keep the heavy metal pollution under control and to take remedial actions in time.

6]Proper landuse may control the pollution and improve the situation.

Pollution affects landuse and landuse affects the behaviour of the pollution. This mutual relationship may be used to find optimal combinations. The possibilities to solve environmental problems by using the land must be further explored, for instance by integrating phytoremediation in agricultural practice.

7]Registration, temporary storage and distribution of excavated soil and sinters.

Sinters were landfilled and used as surface material all over the Kempen. The inventory of locations is still not complete. During activities large amounts of polluted soil may also be excavated, temporarily stored, reused or cleaned. In the past decisions about these activities were made on an ad hoc basis, often with large costs for investigation of the excavated materials. A single organization which coordinates the handling of these materials may save time and money. Expedient procedures will stimulate excavation and proper landfilling of sinters that are still an important source of secundary pollution of soil and groundwater.

CONCLUDING REMARKS

The Kempen is not a really dangerous place to live in, but the soil pollution will need permanent attention by the authorities. The risk and landuse management approach presented above may provide a sustainable solution for the regional soil problems in the Kempen if coordination between the provincial, municipal and water authorities succeeds and the integration of different policies for the area is feasible. Another issue is that the approach cannot be applied without further research. Applied research must be an integral part of the management approach. This is the best way to assure that research will yield the right answers to riks and landuse management questions.

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IN-SITU IMMOBILISATION TECHNIQUES TO REMEDIATE CADMIUM-CONTAMINATED AGRICULTURAL SOILS

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Key words: agriculture, availability, bioavailability, clay, plants, sludge

SUMMARY

This study investigated low-cost Cd remediation options for saline soils using urban and industrial by-products, particularly those from the ferrous- and alumina-smelting industries. Potatoes (*Solanum tuberosum* L.) were grown in soils treated with a range of smelter wastes, biosolids and clays. Cadmium concentrations in tubers were significantly decreased by the biosolids application, despite this treatment adding significant amounts of Cd to the soil. Some smelter wastes were also successful in reducing tuber Cd concentrations. These materials represent a low-costs remediation option for Cd-contaminated agricultural soil.

Contaminated Soil '98, Thomas Telford, London, 1998, 453–460

INTRODUCTION

Cadmium (Cd) accumulation in agricultural soils is a concern in many countries. The rate of soil contamination is usually slow compared to industrial contamination (usually <30 g ha^{-1} yr^{-1}) and cadmium concentrations in soil are usually not high varying from 0.1-1.0 mg kg^{-1} in agricultural soils not receiving sewage biosolid wastes, up to 3 mg kg^{-1} where sewage wastes are used. While these concentrations are not high by standards used to assess contaminated sites in urban areas, they are sufficiently high to cause concerns due to food chain contamination (McLaughlin *et al.,* 1996; Jinadasa *et al.,* 1997). Furthermore, due to the generally low land values in agricultural areas compared to urban and industrial land, remediation techniques must be low cost and integrated into crop production cycles. In Australia, soil salinisation has increased transfer of Cd through the food chain (McLaughlin *et al.,* 1994) so farmers are seeking remediation techniques to minimise Cd accumulation in crops.

Many urban and industrial wastes must be disposed of to landfill, wasting the value inherent in many of these materials. For example, ferrous and alumina smelter by products have many characteristics which could improve agricultural soil productivity. Light-textured soils can have their nutrient retention capacity improved by addition of iron, manganese or aluminium oxides. These materials also have the ability to bind toxic heavy metals into forms unavailable for plants and microorganisms.

This study investigated low-cost Cd remediation options for saline soils using urban and industrial by-products, particularly those from the ferrous- and alumina-smelting industries.

Materials and methods

A glasshouse experiment was performed using potatoes (*Solanum tuberosum* L.) as the test crop. A total of thirteen (13) soil amendments were chosen on the basis that they were inexpensive materials with the potential to significantly reduce availability of Cd to plants, principally through increasing the sorption capacity of the soil for Cd under conditions of high salinity. The materials were a mixture of by-products slags, dusts and muds from the ferrous- and alumina-smelting industries, a natural clay (palygorskite), sewage biosolids and sand-washing clays (Table 1).

The soil used was an Alfisol with sandy texture, having a neutral pH, a low cation exchange capacity (CEC), and a Cd concentration typical of horticultural soils in Australia (McLaughlin *et al.,* 1997).

The soil was air dried and 15 kg dry soil was sieved (<5 mm) into 300 mm diameter, free draining pots. Treatments were thoroughly mixed with the soil at rates equivalent to 5 and 25 t ha^{-1}. The soil was wetted up to -10kPa moisture potential and incubated for 4 weeks prior to planting. The soil was then removed from the pot and nitrogen (N, as ammonium nitrate), phosphorus (P, as superphosphate) and potassium (K, as potassium sulfate) were thoroughly mixed with the soil at rates equivalent to 100 kg N ha^{-1}, 75 kg P ha^{-1} and 150 kg K ha^{-1}. After basal fertilisation, approximately two thirds of the soil was replaced into the pot.

In each pot, one seed potato tuber (*Solanum tubersosum* cv. Atlantic) was planted to a depth of 2-3 cm, after which the pots were placed in a glasshouse. For each pot, the remaining soil

was added when the plants were 20-25 cm tall to minimise the risk of tubers developing above the soil surface. Nitrogen and K were applied as side-dressings 2-3 times during the growth period to ensure these nutrients did not limit growth or yield responses. During growth, each plant was supported by a trellis and pots were watered according to plant demand.

Table 1. Chemical composition of soil and remediation materials used (BF=blast furnace, SWC=sand-washing clay).

	EC	pH_w	Total C	Total P	Oxalate	
					Al	Fe
	dS/m		%	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Soil	0.5	6.79	1.25	398	400	3300
Lime	0.21	8.84	nd	1236	nd	nd
Fe fine slag	1.2	11.9	7.5	2085	2800	92400
Fe dust 1	14.4	11.78	8.5	913	1200	180700
Fe dust 2	12.76	12.55	0.71	680	400	267500
Fe slag medium	8.75	12.65	0.38	5671	3700	71800
Fe slag rough	3.3	12.54	0.58	4779	5900	74300
BF Fe dust	3.34	5.77	0.93	549	500	160100
BF Fe flue dust	7.66	7	17.8	358	1900	85300
BF Fe slag 1	1.02	11.3	0.14	104	19000	1900
BF Fe slag 2	6.23	12.4	1.07	3690	3000	46500
Palygorskite	0.23	9.06	0.41	62	900	400
SWC	0.74	8.52	0.24	164	1000	1500
Biosolids	7.89	7.2	22.3	18828	22300	8500
Al-red mud	4.95	11.62	1.04	481	7900	10500

nd = not determined.

After plant maturity and when haulms had senesced, the tubers were harvested and a soil sample was collected for chemical analysis. Plant tops were separated from roots, and shoot material was washed in deionised water prior to drying at 70°C and recording of dry weights. Tubers were also washed and weighed prior to chemical analysis.

Elemental concentrations in plant shoots and tubers were determined as outlined by McLaughlin *et al.* (1994).

Soil and amendment pH and electrical conductivity (EC) were determined in a water suspension of soil using a 1:5 soil:solution ratio (Rayment and Higginson 1992). Total carbon (C) was determined using a Leco™ furnace. Cation exchange capacity was determined using NH_4Cl leaching procedure (Method , Rayment and Higginson 1992). Phosphorus (P) was extracted from soils using the method of Colwell (1963) and concentrations of P in extracts were determined using the method of Murphy and Riley (1962). Iron (Fe) and aluminium (Al) were extracted from amendments using acidic

ammonium oxalate to estimate the concentrations of amorphous oxide material (Tamm, 1943).

Total and extractable metal concentrations in soils and amendments were determined using the following methods:

1) Total metals - total Cd concentrations in soil were determined by boiling 2 g soil with 8 ml aqua regia (HNO_3:HCl, 3:1 ratio) at 110°C for 2 hours. The mixture was cooled, diluted to volume with 0.08 M HNO_3 and filtered through a 0.22 μm filter prior to spectroscopic analysis by inductively-coupled plasma atomic emission spectroscopy (ICP-AES) or graphite furnace atomic absorption spectroscopy (GFAAS).

2) DTPA-extractable Cd, Cu and Zn - soils were extracted using DTPA (diethylenetriaminepentaacetate) according to the method of Lindsay and Norvell (1979).

Results and Discussion

The materials contained a range of heavy metals (Table 2).

Table 2. Concentrations of metals in the amendments.

	Al	Fe	Mn	Cd	Cu	Ni	Pb	Zn
	%	%	%	----------		mg kg^{-1}	----------	
Soil	0.9	1.0	0.06	0.1	6	3.8	<9	21
Lime	0.1	0.3	0.04	0.2	10	3.3	<9	25
Fe fine slag	0.7	31.2	1.64	0.0	30	9.9	<9	69
Fe dust 1	0.2	44.8	3.32	32.8	70	23.9	635	10104
Fe dust 2	0.1	58.6	1.00	1.3	64	20.1	101	1959
Fe slag medium	1.0	1.7	4.03	0.2	9	2.7	<9	43
Fe slag rough	1.6	2.3	4.00	0.1	11	2.5	<9	22
BF Fe dust	0.1	59.6	0.16	0.1	55	24.3	105	2225
BF Fe flue dust	0.5	41.9	0.10	1.0	38	8.9	638	5548
BF Fe slag 1	5.1	0.5	0.34	0.0	3	<2.2	15	25
BF Fe slag 2	1.0	15.8	2.74	0.1	9	5.9	<9	67
Palygorskite	4.8	2.3	0.05	0.0	16	31.6	14	18
SWC	9.3	3.2	0.01	0.0	16	21.4	37	30
Biosolids	4.3	1.7	0.02	9.8	1001	70.3	445	1816
Al-red mud	5.3	36.0	0.08	0.0	50	5.4	20	42

As expected, all the alumina and ferrous-smelting by products were very high in iron (Fe) with Fe concentrations up to 60% in the blast furnace dusts. Cadmium concentrations were low in all materials except Fe dust 1, which was a dust derived from air filtration units at a steel smelter, and in sewage biosolids. The biosolids were also very high in copper (Cu) compared to other materials (Table 2).

Plant growth was not significantly affected by the amendments (data not shown). Cadmium uptake was significantly reduced by some of the treatments, particularly Cu-enriched water treatment sludges and sewage biosolids, and alkaline (non-calcareous) clays (Figure 1).

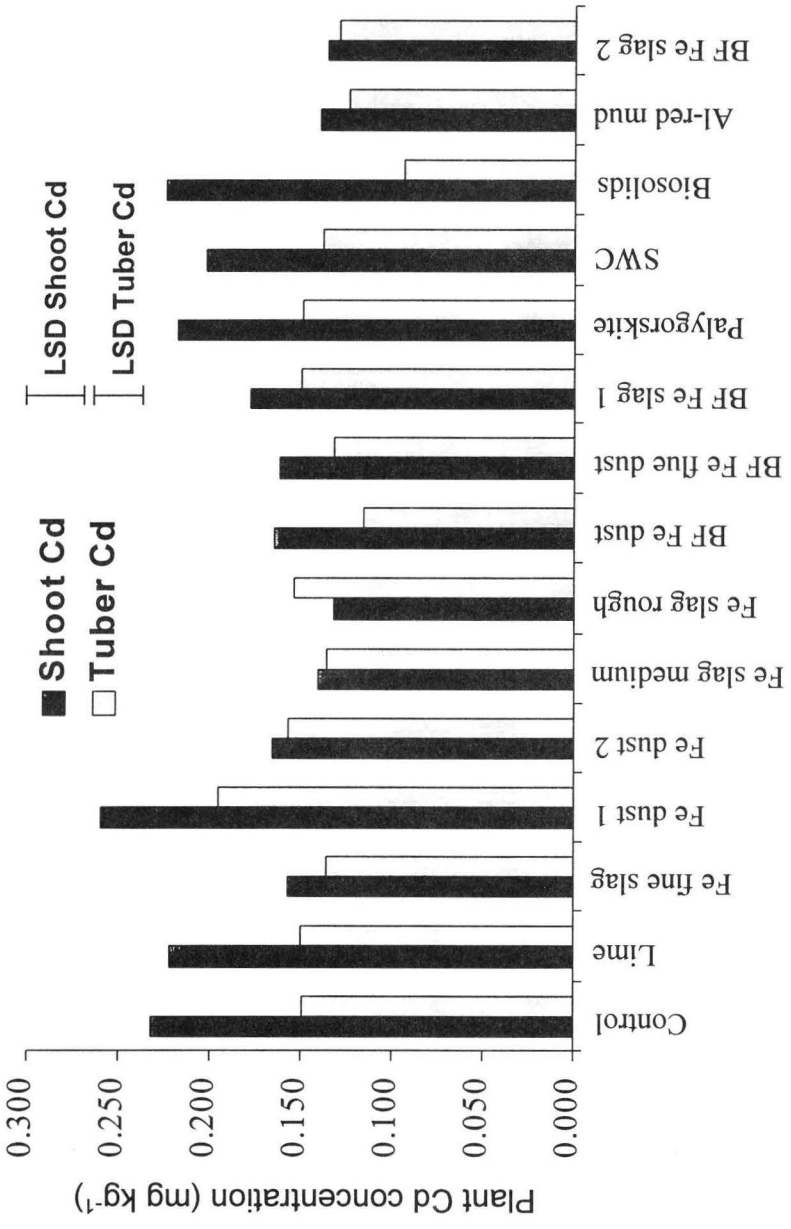

Figure 1. Effect of soil amendments on Cd concentration in potato shoots (dry weight basis) and tubers (fresh weight basis).

Cadmium concentrations in crops treated with Fe dust 1 was actually increased, probably due to the high Cd present in this material. While sewage biosolids had high Cd concentrations, Cd concentrations in crops treated with this material were actually decreased. This may have been due to increased retention of Cd by organic matter added in the biosolids, or could have been due to the high Cu present in this material. In recent experiments in our laboratory, Cu has been found to be antagonistic to Cd uptake by potatoes (McLaughlin *et al.*, unpublished data).

Uptake of Cu, Mn, P and Zn into plant shoots and tubers was also significantly affected by the amendments (Table 3). Concentrations of DTPA-extractable Cd, Cu and Zn in soils are shown in Table 4. Plants growing on soils treated with sewage biosolids took up more Cu (and less Cd) than other plants (Table 3), in line with increased levels of DTPA-Cu and sodium bicarbonate-extractable P (Table 4).

Table 3. Concentrations of copper, manganese, phosphorus and zinc in potato shoots.

	Tuber				Shoot			
	mg kg^{-1}		%	mg kg^{-1}	mg kg^{-1}		%	mg kg^{-1}
	Cu	Mn	P	Zn	Cu	Mn	P	Zn
Control	6.6	7.6	0.41	26	5.5	70	0.36	51
Lime	5.9	8.1	0.34	22	5.1	43	0.23	22
Fe fine slag	5.1	8.0	0.32	21	3.8	55	0.19	20
Fe dust 1	9.4	14.8	0.35	33	6.3	186	0.24	103
Fe dust 2	6.6	7.0	0.36	27	4.8	29	0.24	44
Fe slag medium	7.2	10.5	0.37	16	5.7	72	0.27	16
Fe slag rough	5.8	9.6	0.33	13	4.9	75	0.25	15
BF Fe dust	6.5	8.8	0.39	30	5.0	81	0.26	83
BF Fe flue dust	9.4	9.4	0.42	36	5.9	95	0.29	126
BF Fe slag 1	6.3	7.4	0.36	25	5.1	31	0.27	38
BF Fe slag 2	5.2	8.1	0.34	14	4.9	57	0.23	17
Palygorskite	6.6	7.9	0.42	26	4.3	66	0.34	45
SWC	6.7	8.5	0.40	29	4.2	45	0.31	50
Biosolids	13.7	8.3	0.43	29	15.4	81	0.44	82
Al-red mud	7.0	8.1	0.36	25	5.3	28	0.23	33
LSD	1.7	1.9	0.05	3	1.9	27	0.06	11

Concentrations in shoots were below levels found to be phytotoxic (Huett *et al.*, 1997). Manganese concentrations were high in plants treated with Fe dust 1 and the medium and coarse Fe slag materials, in line with the high total manganese concentrations in these materials (Table 2). All the smelter-derived materials significantly reduced uptake of P into plant shoots, probably due to increased retention of P by the oxides in these materials, and this was reflected to some extent in reduced concentrations of sodium bicarbonate-extractable P in soils at harvest. Biosolids enhanced P uptake and increased sodium

bicarbonate-extractable P in soil. Growth was unaffected by these varying P concentrations. Concentrations of Zn in shoots of plants treated with Fe dust 1, blast furnace dust (BF Fe dust) blast furnace flue dusts (BF Fe Flue dust) and biosolids were significantly increased over control values. Similar increases were noted in concentrations of DTPA-extractable Zn in these same treatments.

Table 4. Concentrations of DTPA-extractable Cd, Cu and Zn and $NaHCO_3$-extractable P (Bic-P) in soils at harvest.

	pH	DTPA			Bic-P
		Cd	Cu	Zn	
		---------- mg kg^{-1} ----------			
Control	5.9	0.09	1.00	2.3	121
Lime	7.7	0.03	0.76	1.5	129
Fe fine slag	7.4	0.05	0.71	1.5	115
Fe dust 1	6.4	0.34	0.89	36.6	106
Fe dust 2	4.5	0.08	0.81	2.7	111
Fe slag medium	8.1	0.05	0.67	1.3	171
Fe slag rough	8.0	0.05	0.71	1.3	166
BF Fe dust	6.0	0.07	0.96	6.3	108
BF Fe flue dust	6.2	0.09	0.93	22.7	118
BF Fe slag 1	7.0	0.06	0.76	1.5	119
BF Fe slag 2	7.9	0.04	0.72	1.6	154
Palygorskite	5.8	0.08	0.90	2.0	111
SWC	5.9	0.08	0.96	1.9	111
Biosolids	6.2	0.15	4.51	12.7	153
Al-red mud	6.7	0.06	0.84	1.7	103
LSD	1.1	0.01	0.10	0.51	8

Conclusions

Smelter wastes are possible low-cost ameliorants for reducing Cd concentrations in agricultural crops on saline soils. In association with other agronomic strategies to manage Cd transfer through the food chain(McLaughlin *et al.*, 1996), re-use of these materials on soils presents a low cost disposal option for these industries.

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INTEGRATED LEACHING PROCESSES FOR THE REMOVAL OF HEAVY METALS FROM HEAVILY CONTAMINATED SOILS

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Key words: Heavy metals, lead, soil, decontamination techniques, remediation, leaching

SUMMARY

A long-term solution to the remediation of soils contaminated by heavy-metals may be the permanent removal of pollutants using chemical treatment (leaching) methods. To this end, three alternative leaching processes based on the use of citric acid, Na_2EDTA and HCl-$CaCl_2$ are examined. Integrated flowsheets are designed and evaluated experimentally, including leaching of the soil, removal of metals from the aqueous solution and regeneration of the leaching reagents. The economic and environmental implications from the implementation of such processes are finally discussed.

KURZFASSUNG

Eine langfristige Lösung für die Sanierung von Böden, die mit Schwermetallen kontaminiert sind, kann die ständige Entfernung der Schadstoffe mittels physikalischen oder chemischen Behandlungs-(Auslauge-) verfahren sein. Zu diesem Zweck werden drei alternativeAuslaugeverfahren überprüft, die sich auf die Verwendung von Zitronensaüre, Na_2EDTA und HCl-$CaCl_2$ stützen. Integrierte Fließdiagramme, enthaltend Bodenauslaugung, Metalentfernung von der Wasserlösung und Regenerierung der Auslaugereagenzien, werden entworfen und experimentell bewertet. Die ökonomische und Umwelt-Auswirkungen bel der Durchführung solcher Prozesse werden schließlich diskutiert.

RÉSUMÉ

Une solution à long terme pour l' assainissement des sols pollués par des métaux lourds est l' extraction permanente des polluants en appliquant des méthodes de traitement chimique. A ce propos, trois procédés de lixiviation alternatives, comprenant l' utilisation d' acide citrique, Na_2EDTA et HCl-$CaCl_2$, ont été examinés: Des flowsheets integrés ont été conçus et évalués expérimentalement, comprenant la lixiviation du sol, la séparation des métaux par la solution aqueuse et la régénération des réactifs lixiviants. Les implications économiques et environnementales par l' application de tels procédés sont finallement discutées.

Contaminated Soil '98, Thomas Telford, London, 1998, 461–470

1. INTRODUCTION

The removal of heavy metals from contaminated soils applying leaching techniques is a promising soil remediation option since it provides a permanent solution to the environmental problem.

Many research efforts have been done for the development of leaching processes, but no large-scale applications have been reported. Leaching has been practised with inorganic or organic acids, such as: hydrochloric (Roche et al, 1994), sulphuric (Jenkins et al, 1981), nitric (Royer et al, 1992) and acetic acid (Krishnamurthy, 1992). For soils contaminated with lead, many studies have been carried out using the disodium or tetrasodium salt of EDTA (ethylenediaminetetraacetic acid, $C_{10}H_{16}N_2O_8$) (Elliot et al, 1989; Peters and Shem, 1992). The use of an acidified brine (HCl-$CaCl_2$) has been proposed for a site contaminated mainly with zinc (Roch et al., 1995).

The successful implementation of leaching processes does not only rely on the efficient removal of metals from soils. An integrated process includes additional treatment stages, which must be optimised in order to obtain a soil remediation technique environmentally and economically acceptable:

a) Metals should be removed from the leachate and recovered in the form of a low volume solid residue, appropriate for disposal in a hazardous waste landfill area or even for recycling in the metallurgical industry.
b) In most cases the leaching solution, should be further treated, for regeneration and reuse in the leaching stage, or for final polishing in order to produce an acceptable liquid effluent for disposal in natural waters.

Most of the conventional techniques have been tested for the removal of metals and the regeneration of leaching solutions, including: precipitation with $Ca(OH)_2$, Na_2CO_3 (Jenkins et al, 1981) or Na_2S (Bricka et al, 1993); electrochemical recovery (Allen and Chen, 1993) etc. The results are however contradictory regarding the efficiency and applicability of the proposed techniques, especially for the processes based on the use of organic acids and chelators.

Despite the intense research activity for the development of individual unit operations, an overall evaluation of the corresponding integrated processes, regarding their environmental compatibility and cost effectiveness is missing. An integrated approach has been attempted in this paper for three alternative leaching processes based on the use of citric acid, EDTA and HCl-$CaCl_2$.

2. MATERIALS AND METHODS

2.1 Characteristics of treated material

Leaching tests were carried out on a heavily contaminated material from Lavrion, Greece. The chemical composition is given in Table 1, together with the Netherlands "C" standards, which indicate soils needing remediation. The U.S. EPA (1986) Toxicity Characterisation Leach Procedure (TCLP) was applied to evaluate the toxicity of the soil. The results are included in Table 1 together with the regulatory limits (in parentheses).

Table 1
Chemical composition of the soil.

Element	Weight in soil, %	Netherlands "C" standards, ppm	U.S.EPA TCLP test, ppm	
Pb	3.48	600	310	(5)
Zn	2.02	3000	320	(-)
Cd	0.01	20	2.85	(1)
As	0.28	50	1	(5)
Ca	7.28	-	-	
Fe	6.00	-	-	
Mn	0.35	-	-	

2.2 Leaching tests

The selection of leaching reagents was mainly based on the chemistry of Pb, which is the key-contaminant in Lavrion soils. Lead (Pb) is a metal which is not soluble in the common inorganic acids used in the hydrometallurgical processes, such as H_2SO_4 and HCl, due to the formation of the corresponding insoluble salts, $PbSO_4$ and $PbCl_2$. On the other hand, it has a strong affinity for complexation and chelation. For these reasons the reagents evaluated during this experimental work were : citric acid, a natural organic acid with chelating capabilities, the strong chelator EDTA and an acidic chloride solution of HCl and $CaCl_2$.

The performance of citric acid (0.33M) and Na_2-EDTA (0.25M) was evaluated with leaching tests at ambient temperature, in 500 ml spherical stirred reactors at 1:10 solid/liquid ratio. Leaching has been applied at two stages; the solid residue of the first stage was filtered, washed and subjected to a second leaching treatment with fresh solution. The duration of each stage was 24 hours.

Column leaching has been used for the $CaCl_2$-HCl system. Approximately 5.4 kg of the material was placed in a plexiglass column of 10cm diameter to form a bed of 50 cm height. The leaching solution, containing 0.25 M HCl and the required quantity of $CaCl_2$ to obtain a total chloride concentration of 4M, was fed to the top of the column at a flowrate of 0.6 L/d. Leaching lasted for 260 days and a total amount of 156 liters were supplied.

2.3 Removal of metals from the leach solutions

Resin adsorption of heavy metals has been tested for the citric acid and EDTA solutions. A strongly acidic cationic resin (DOWEX 50WX8), with sulphonic acid groups and a nominal capacity of 1.9 eq/L, was used for citric acid. For the case of Na_2EDTA leach solution, the strongly acidic cationic resin was inappropriate, as it led to EDTA acid precipitation. The tests were carried out using a weakly acidic cationic resin, comprising carboxylic groups (DOWEX CG-5OI, capacity 3.5 eq/L).

Removal of metals with precipitation techniques was evaluated for all three leaching systems. The reagents used include NaOH, $Ca(OH)_2$, Na_2S and Ultra-Clear, a commercial product containing sodium dimethyldithiocarbamate, $(CH_3)_2NCS_2Na$. The experiments were carried out in beakers at atmospheric conditions and under continuous agitation. The reagents were added to the solution stepwise at predetermined quantities. The pH was continuously measured and aliquots were taken to follow the progress of precipitation as a function of the reagent dose.

3. RESULTS AND DISCUSSION

3.1 Leaching

The results of the leaching tests are summarised in Table 2. It is obvious that the above leaching systems can achieve high extraction rates for the main metal contaminants, Pb, Zn and Cd, while As remains unaffected. Citric acid was capable to remove 66% of Pb, 73 % of Zn and 92% of Cd. EDTA has improved Pb removal up to 80%. Best results finally were obtained with the HCl-$CaCl_2$ system, with removal rates exceeding 90% for all Pb, Zn and Cd. These results suggest that the highly acidic conditions, prevailing during the HCl-$CaCl_2$ leaching can dissolve species which are refractory to the chelating action of EDTA and citrate.

In order to evaluate the efficiency of leaching treatment on the quality of residual soil the EPA-TCLP test was applied and the results are presented in Table 2. Leaching treatment has resulted in removing the mobile and hazardous species of toxic elements and the residual soil is essentially characterised as non-toxic. In several countries however the regulatory criteria for treated soil are based on total metal concentration. Despite the high extraction rates, it was impossible to reduce *total* residual concentrations below the Netherlands 'C' standards even with the most efficient leaching system, HCl-$CaCl_2$.

Table 2
Metal extraction during the leaching tests

	Pb	Zn	Cd	As	Ca	Mg	Al	Fe_{tot}	Mn
Initial Soil, mg/kg	34800	20200	100	2800	72800	15200	12900	60000	3500
Citric acid (H_3C)									
[a]3.3 moles H_3C/kg soil, Extr., %	54.6	61.4	72.0	3.6	65.2	37.5	9.3	3.5	74.3
[b]6.6 moles H_3C/kg soil, Extr., %	66.1	72.8	92	10	70.9	53.3	12.1	5.5	86
TCLP of residue, mg/L in leachate	4.8	14.6	0.08	<1					
Na_2EDTA (Na_2H_2L)									
[a]2.5 moles Na_2H_2L /kg soil, Extr., %	75.6	55.4	96.0	21.0	78.7	6.4	6.3	2.8	82.9
[b]5.0 moles Na_2H_2L /kg soil, Extr., %	79.9	67.8	100	26.1	82.6	6.7	7.9	4.2	90.0
TCLP of residue, mg/L in leachate	5.3	25.6	0.17	<1					
HCl-$CaCl_2$									
[c]5.6 moles HCl/kg soil, Extr., %	88.1	87.8	87.4	0.01		88.1		1.4	93.0
[d]6.7 moles HCl/kg soil, Extr., %	91.1	91.3	91.8	6.1	91.7	93.9	47	7.0	94
TCLP of residue, mg/L in leachate	<0.5	0.26	<0.02	1					

[a] Stirred reactor : amount of leaching reagent supplied per kg soil during the 1st leaching stage
[b] Stirred reactor : total amount of reagent supplied per kg soil during the two leaching stages
[c] Column test : amount of HCl corresponding to the neutralisation potential of the material
[d] Column test : Total amount of HCl

3.2 Removal of metals from leach solutions

The results concerning the removal of metals from the citric acid leach solution are shown in Table 3. The cation exchange treatment was found to remove efficiently the

metals from the leach solution. Precipitation with NaOH was inefficient; a very high excess of NaOH, 6.5 greq/L, was required in order to observe the initial formation of precipitates. Better results were obtained using lime. An amount approximately equivalent to the normality of the solution, 1.1 greq/L $Ca(OH)_2$, was sufficient to remove more than 99% of all the metals examined.

Resin treatment and neutralisation with NaOH, were found to be inefficient for the removal of heavy metals from the EDTA solution (Table 4). On the contrary lead, zinc and cadmium were efficiently removed as sulphides, while Ca was partially precipitated.

Table 3

Removal of metals from the citric acid leach solution, 0.33 M (1N)

		(mg/L)								
	pH	**Pb**	**Zn**	**Cd**	**As**	**Ca**	**Mg**	**Al**	**Fe**	**Mn**
Initial solution	2.8	1900	1240	7.2	10	4750	570	120	210	260
Treatment with a strongly a stronlgy acidic resin (DOWEX 50WX8)										
Treated solution		bdl	bdl	bdl		0.1	bdl	bdl	bdl	bdl
Precipitation with NaOH										
6.5 greq NaOH /L sol.	>12.5	760	1000	0.2	0				21.4	14.8
7.6 greq NaOH /L sol.	>12.5	900	1140	0.5	4	240	40.2	29.8	1.8	5.6
Precipitation with $Ca(OH)_2$										
1.1 greq $Ca(OH)_2$/L sol.	-	13	8	0.1	0		5.4	32.1	0.5	1.7
2.2 greq $Ca(OH)_2$/L sol	-	16	9	0.1	0		4.2	28.7	8.0	1.1

Table 4

Removal of metals from the EDTA solution, 0.25 M

		(mg/L)								
	pH	**Pb**	**Zn**	**Cd**	**As**	**Ca**	**Mg**	**Al**	**Fe**	**Mn**
Initial solution	5.3	2630	1120	9.63	59.0	5730	97.1	80.9	170.0	290.0
Treatment with a strongly a weakly acidic resin (DOWEX CG-5OI)										
Treated solution		2610	980	8.84					161.5	280
Precipitation with NaOH										
0.32 greq NaOH /L sol.	13.3	2506	1102	8.46	0.0	5170	59.2	69.5	6.4	237.6
1.00 greq NaOH /L sol.	>13.5	2470	1050	9.45	55.0	5020	35.7	75.9	5.5	190.0
Precipitation with Na_2S										
0.1 moleNa_2S/L sol.	9.7	0	968.0	0.32	58	4059			143.0	269
0.2 mole Na_2S/L sol	12.6	0	3.6	0.38	57	4104			96.5	269

Table 5

Lime precipitation of metals from the $CaCl_2$ solution, Cl_{tot}=4 M

pH	Add.$Ca(OH)_2$ g/1000mL	Pb (ppm)	Zn (ppm)	Cd (ppm)	Mn (ppm)	Mg (ppm)
4.4	0	1723	2393	9.95	437	1014
6.0	0.6	1605	2403	9.97	488	1045
7.0	2.5	280	783	9.39	427	999
8.0	3.6	27.2	27	8.77	202	918
8.5	4.0	15.4	5.63	7.55	12.6	805
9.0	4.5	**13.4**	3.16	6.23	**0.8**	541
10.0	6.1	210	**1.29**	3.13	0.8	17.6
11.0	9.0	167.4	331	3.33	23.9	**0.8**
11.2	14.5	225	817	**1.34**	41.7	1.5

Treatment with lime has been used for the removal of metals from the $CaCl_2$ solution and the experimental results are shown in table 5. It should be mentioned that the selection of this salt to provide the required chloride matrix during the leaching stage, instead of other alternatives, i.e. NaCl, $MgCl_2$, was mainly based to the fact that lime is a cheap and efficient reagent for the subsequent metals removal step. From the results shown in Table 5 it is seen that Pb, Zn and Mn are efficiently removed at pH 9. Increasing precipitation pH to the value of 11, improves the removal of Cd and Mg but the Pb and Zn hydroxides are partially redissolved due to the formation of hydroxocomplexes, i.e. $Pb(OH)^{3-}$, $Zn(OH)^{3-}$, at this alkaline pH.

3.3 Proposed treatment stages

The treatment steps and the stoichiometry of the reactions involved in the three processes are summarised in table 6. Lead carbonate, $PbCO_3$, is considered as the typical pollutant to be removed from the soil. Similar equations can be written for the other metal species interfering in the process. For the leaching systems which are based on the use of citric acid and EDTA, it was thought more appropriate to investigate process flowsheets comprising *complete regeneration and recycling* of the leaching solution. It is thus possible to avoid production of liquid effluents with a high organic load which are not likely to be accepted for final discharge.

Citric acid process

The use of a strongly acidic cationic resin for the removal of metals from the citric acid leach solutions seems to be a technically feasible alternative, as it gives removal rates near 100%. Moreover the product is a regenerated acid solution that can be recycled directly to the leaching stage. Metals however should be removed from the resin and recovered in a low volume final residue appropriate for disposal. An integrated flowsheet should thus comprise the following treatment steps :

Table 6
The stoichiometry of the reactions involved in the three leaching processes

Citric acid process		
Leaching	$H_3C + PbCO_3 = HPbC + CO_2 + H_2O$	(1)
Metals adsorption	$2HR + HPbC = PbR_2 + H_3C$	(2)
Resin regeneration	$2HCl + PbR_2 = PbCl_2 + 2HR$	(3)
Final metals recovery	$Ca(OH)_2 + PbCl_2 = \mathbf{Pb(OH)_2 + CaCl_2}$	(4)
	(where C= citrate ligand and R=strongly acidic resin)	
Na_2EDTA process		
Leaching	$Na_2H_2L + PbCO_3 = Na_2PbL + CO_2 + H_2O$	(5)
Metals precipitation	$Na_2S + Na_2PbL = Na_4L + \mathbf{PbS}$	(6)
EDTA regeneration	$2HR + Na_4L = 2NaR + 2Na_2H_2L$	(7)
Resin regeneration	$2HCl + 2NaR = 2HR + \mathbf{2NaCl}$	(8)
	(where L= EDTA ligand and R=weakly acidic resin)	
HCl-$CaCl_2$ process		
Leaching	$2HCl + PbCO_3 = PbCl_2 + CO_2 + H_2O$	(9)
Metals precipitation	$Ca(OH)_2 + PbCl_2 = \mathbf{Pb(OH)_2 + CaCl_2}$	(10)

Characters in italics denote the reagents and those in bold the effluent streams of the processes

1. Leaching of the contaminated material (reaction 1)
2. Removal of metals from the leachate with resin treatment and recycling of the regenerated leaching solution (reaction 2)
3. Regeneration of the strongly acidic resin, i.e. with HCl (reaction 3)
4. Recovery of the metals from the HCl solution, i.e. by precipitation with $Ca(OH)_2$ (reaction 4).

The main reagents consumed in this conceptual flowsheet are HCl and $Ca(OH)_2$, for the regeneration of the resin and the precipitation of the metals. The final effluents are the sludge of metal hydroxides and the $CaCl_2$ solution, produced during the fourth step. The final precipitation step for the recovery of metals is similar to the one included in the chloride process.

Na_2EDTA process

Recycling is crucial for the EDTA process due to the high cost of this reagent. During leaching the initial acidity is consumed (reaction (5), table 6) and the precipitation treatment with Na_2S, results in a final alkaline solution containing an excess of Na^+ ions in comparison with the initial leaching reagent. The regeneration of the initial acidity could be achieved using a weakly acidic resin following reaction (7) in Table 6.

A test was carried out on the EDTA solution emanating from the Na_2S precipitation treatment. The results are shown in Table 7. As seen, the resin adsorbs only part of the Na^+ ions, while Ca^{2+} ions remain unaffected. The regenerated solution contains less H^+ from the original (0.35 as against 0.5 mole/L). It is therefore expected that its activity regarding leaching will be reduced. Although essentially complete recovery of EDTA has been achieved, 40% of the EDTA in the final solution is associated with calcium; it is expected however that Ca-EDTA will be able to dissolve lead as the Pb-EDTA complex is thermodynamically more stable ($\log K_{Ca\text{-}EDTA}$= 12.4, $\log K_{Pb\text{-}EDTA}$= 17.88). Further experimental evidence is needed in order to verify the above hypothesis.

Table 7

Composition of the EDTA solution in mole/L in the initial stage, after precipitation and after regeneration stage.

	Initial	After precipitation	After regeneration
Na_2H_2L	0.25		0.10
NaH_3L			0.05
Na_2CaL		0.10	0.10
Na_4L		0.15	
Na_2S		0.15	

This process comprises the following treatment steps :

1. Leaching of the contaminated material (reaction 5)
2. Removal of metals from the leachate by precipitation with Na_2S (reaction 6)
3. Regeneration of the initial acidity with a weekly acidic resin and recycling of the solution to the leaching stage (reaction 7)
4. Regeneration of the resin with HCl (reaction 8)

The main reagents consumed in the process are NaOH and Na_2S for the precipitation of the metals and HCl for the regeneration of the resin. The final effluents are the sludge of metal sulphides and the NaCl solution, produced during resin regeneration.

Chloride process

In the HCl-$CaCl_2$ process, a solution containing mainly $CaCl_2$ is produced from the precipitation stage (reaction 10, table 6). The major part of this solution can be recycled to the leaching stage in order to maintain the required elevated concentration of chlorides, Cl_{tot}= 4 M. Fresh HCl should be also supplied to compensate for the consumption of acidity during leaching (reaction 9, table 6). As a consequence a liquid stream should be discarded to maintain the overall mass balance. This final $CaCl_2$ effluent should meet the environmental regulations for disposal.

The residual concentrations of heavy metals obtained with the addition of lime (Table 5) exceed the environmental limits. A final polishing step is thus required. Precipitation of the residual metals in the form of sulphides, using Ultra-Clear has been tested. Ultra Clear is a commercial product containing sodium dimethyldithiocarbamate and is proposed in the literature (Roch *et al.*, 1994) as a non-toxic, easy to handle alternative to Na_2S with similar advantages, as it leads to the precipitation of highly insoluble sulphides:

$$PbCl_2 + (CH_3)_2NCS_2Na + 2H_2O \rightarrow 2PbS + (CH_3)_2NCO_2Na + HCl$$

As seen in Table 8, this treatment has resulted in reducing the residual concentrations, but the quality of final effluent is not appropriate for disposal in natural receivers, especially for Pb and Cd. Only the criteria for disposal in sewers have been met.

Table 8

Removal of residual heavy metal concentrations from chloride solutions with Ultra Clear

UltraClear 0.06M (ml)	pH	Pb (ppm)	Zn (ppm)	Cd (ppm)	Mn (ppm)
0	9.56	14.2	3.50	0.70	0.72
10	9.49	4.7	0.67	0.65	0.70
20	9.47	4.6	0.92	0.62	0.69
30		4.5	1.23	0.61	0.67
60	9.66	4.4	1.65	0.55	0.61
Upper permitted concentrations for disposal					
Natural receivers		0.1	2	0.02-0.1	2.0
Sewers		5	20	0.5	10

3.4 Conclusions - Economic and environmental implications

The key factors for the successful implementation of leaching processes are :

- Efficient removal of the metals from the soil to meet the regulatory criteria for treated soil
- Minimisation of liquid and solid effluents and quality within the environmental regulations for disposal.
- An affordable cost

Preliminary mass balance calculations were performed in order to obtain a first estimation regarding (a) reagents consumption and costs and (b) volume of the

produced effluents for each one of the above processes. The results are summarised in Table 9. It must be underlined that only stoichiometric consumptions are included. Process losses due to solid/liquid separation or washing operations are excluded for the time being.

Table 9

Crucial quantities per t soil for the three leaching processes

METALS EXTRACTED DURING LEACHING TESTS

		Quantity of leaching reagent kmol/t soil	Metals extracted Total kmol/t soil	Metals extracted Ca kmol/t soil
Citric acid				
	1 stage	3.3	1.9	1.3
	2 stages	6.6	2.2	1.4
Na_2EDTA				
	1 stage	2.5	2.0	1.6
	2 stages	5.0	2.2	1.7
HCl-$CaCl_2$				
	pH ≈ 3	5.6	2.7	1.8
	pH < 1	6.7	3.1	1.9

STOICHIOMETRIC REQUIREMENTS OF REAGENTS AND RELATED COSTS

	Precipitation reagent		Acid		TOTAL	Cost due to Ca diss.
	kmol/t soil	GRD/t soil	keq/t soil	GRD/t soil	GRD/t soil	GRD/t soil
	$Ca(OH)_2$		*HCl*			
Citric acid	0.8 (a)	2842	4.5	18652	**21494**	*12020*
	Na_2S					
Na_2EDTA	2.2 (b)	30030	4.4	18238	**48268**	*36201*
	$Ca(OH)_2$					
HCl-$CaCl_2$	1.5 (c)	5150	6.6	27357	**32507**	*15334*

(a) 1.4 kmol of Ca /t soil in liquid effluents — $Ca(OH)_2$: 48 GRD/kg = 3552 GRD/kmol
(b) 1.7 kmol of Ca/t soil in sulphides sludge — Na_2S : 175 GRD/kg = 13704 GRD/kmol
(c) 1.9 kmol of Ca /t soil in liquid effluents — HCl 33% : 38 GRD/kg = 4145 GRD/kmol

Note : 1 GRD = 1/310 ECU (Feb 1998)

PROCESS EFFLUENTS TO BE DISPOSED OFF

Metals sludge			
Citric acid	Hydroxides	78 kg/t soil	
Na_2EDTA	Sulphides	186 kg/t soil	(120 kg as Ca_2S)
HCl-$CaCl_2$	Hydroxides	123 kg/t soil	
Liquid effluents			
Citric acid	$CaCl_2$	21 m^3/t soil	10 x Resin Bed Volume (2keq/m^3)
Na_2EDTA	NaCl	22 m^3/t soil	20 x Resin Bed Volume (4keq/m^3)
HCl-$CaCl_2$	$CaCl_2$	1.65 m^3/t soil	Bleed stream equal to HCl make-up

The major disadvantage of all the leaching systems tested during this experimental work is that they were found to attack important soil components, mainly $CaCO_3$ which constitutes more than 20% in the matrix of the examined material. The implications are both economic and environmental. The dissolution of Ca increases the consumption of reagents and its contribution to the related costs is estimated to be approximately 47% for the HCl-$CaCl_2$, 56% for Citric acid and 75 % for the EDTA process. Extracted Ca finally reports to the liquid (HCl-$CaCl_2$, Citric acid) or solid (EDTA) effluents of the processes, maximizing the volume of wastes to be disposed of. Moreover $CaCO_3$ is a useful soil component and its destruction constitutes an undesirable side effect.

It is often reported in the literature that the major advantage in using chelators, is that they remove selectively the heavy metals and preserve the integrity of soil matrix. A substantial dissolution of $CaCO_3$ was however observed during this experimental work. Research activity is currently in progress to evaluate alternative chelators and define optimum operating conditions in order to suppress the dissolution of calcite, which was found to be the major soil component interfering in the process.

Calcite preservation is impossible in the HCl-$CaCl_2$ process. This process however has the benefits of achieving high extraction rates and producing a relatively low volume of liquid effluents.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the European Commission for the financial support of this project under the BRITE EURAM Programme, No. BRPR-CT96-0297.

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ELECTRODIALYTIC SOIL REMEDIATION - IMPROVED CONDITIONS AND ACCELERATION OF THE PROCESS BY ADDITION OF DESORBING AGENTS TO THE SOIL

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Key words: Heavy metals, contaminated soil, soil remediation

SUMMARY

Electrodialytic soil remediation is a technology under development. The method is based on use of an electric current as a cleaning agent and has proved to work in laboratory scale with various heavy metal polluted soils. At present the method is tested on a larger scale. Meanwhile remediation of some soil types and some heavy metal combinations can be improved by adding a desorbing agent to the soil during the remediation action. An example of this is given. Ammonia is added to a calcareous copper polluted soil and both the removal rate and the energy consumption is improved compared to a similar remediation where no ammonia was added to the soil.

Contaminated Soil '98, Thomas Telford, London, 1998, 471–478

INTRODUCTION

The environmental problem of heavy metal polluted soils is of increasing concern. This is due to a greater understanding of the toxicological importance of heavy metals in the ecosystem combined with the lack of methods to remediate such sites.
For these problematic polluted soils several research teams worldwide are developing remediation methods which are based on the fact that soils are electrically conducting. These remediation methods are called electrokinetic remediation methods. The fact that soils are electric conducting has been used for different purposes for decades. As early as in the 1930s investigations were made on removal of sodium from soil by applying an electric field. At about the same time an applied electric field was used to dewater and stabilize soft soils by the pioneer in the field Leo Casagrande. Then in the middle of the 1980s the development of the electrokinetic soil remediation method was initiated by various teams e.g. Geokinetics with Lagemann in the Netherlands and Hamed and Pamucku in the US. These methods are based on applying an electric current to the soil to remove toxic substances.

Electrodialysis is a separation technique that has been used since the 1950s for demineralization of potable water or brackish water and for concentraton of sea water for salt production. The most important elements in electrodialysis are ion exchange membranes and the driving force that is causing the separation is an electric dc current.

Recently the principle of electrodialysis has been suggested for use in remediation of heavy metal polluted soils, too. Electrodialytic soil remediation is a combination of the two technologies: electrokinetic soil remediation and electrodialysis. The method has been developed at the Technical University of Denmark in cooperation with AS Bioteknisk Jordrens.
This paper gives a short description of the method and presents the state of development and the futute work to be done. An example from our laboratory with improved remediation conditions by adding a desorbing agent to the soil during the remediation is given.

ELECTRODIALYTIC SOIL REMEDIATION

When an electric current is applied to a soil the current is carried by ions that are electromigrating through the soil in accordance with their charge. In a heavy metal polluted soil a part of the current is carried by the polluting heavy metals, and this is needed for the remediation to occur.

The principle of the electrodialytic soil remediation method is illustrated by a laboratory cell in Figure 1. The cell consists of five compartments that are separated by ion exchange membranes.

The cathode compartment (I) is separated from the concentration compartment (II) by an anion exchange membrane. This membrane ensures that no metal precipitation will occur on the surface of the cathode making the electrode reaction difficult to controll. The soil compartment (III) and the concentration compartment (II) are separated by a cation

exchange membrane to avoid OH^- ions to enter the soil causing problems with heavy metal precipitation within the soil.
In front of the anode the membranes are placed oppositely. Between the concentration compartment (IV) and the soil compartment (III) an anion exchange membrane is placed. This membrane prevents cations in electromigrating into the soil from the concentration compartment. This is done in order to avoid competition between cations from compartment (IV) and cations originating from the soil. Finally a cation exchange membrane is separating the anode compartment (V) from the concentration compartment (IV). This membrane ensures that no anions that are removed from the soil can enter into the vicinity of the anode. An example of undesisirable ions in the anode compartment is Cl^- ions because this could lead to production of toxic Cl_2 gas.

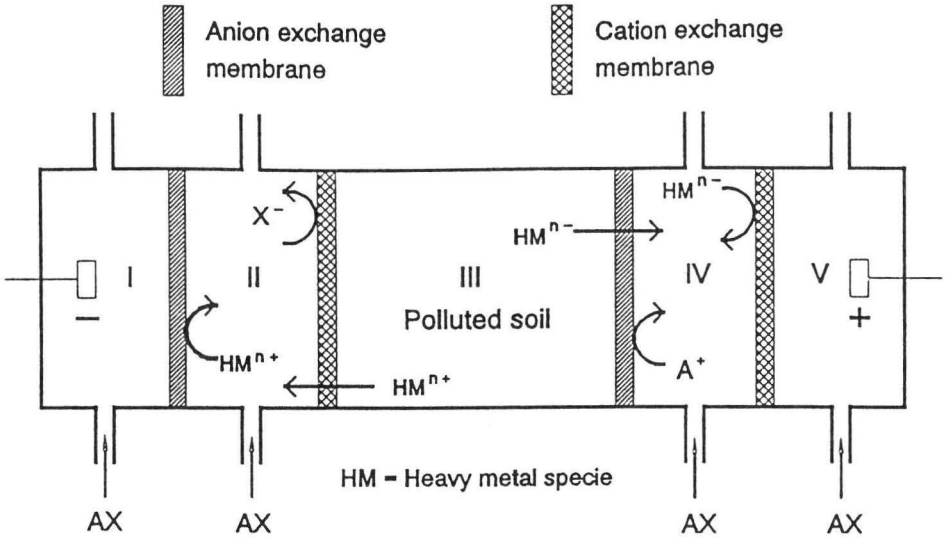

Figure 1: The principle of electrodialytic soil remediation

The ion exchange membranes make it possible to control the remediation process of heavy metal removal. The remediation is ended when the heavy metal concentration throughout the whole soil volume is below a prescribed limit. The heavy metals are now situated and concentrated in the two concentration compartments. Heavy metals removed from the soil as anions are present in compartment (II) and heavy metals removed as cations are found in compartment (IV). The heavy metals are thus present in solution from where different methods, depending on the partikular metal, can be used for further concentration or for isolation of the heavy metals.

PRESENT STATE OF DEVELOPMENT

The development of the electrodialytic soil remediation method was initiated in 1992 (1) and the principle of the method is patented worldwide. The method has been developed at the Technical University of Denmark (DTU), where several departments now are involved in the research (Dept. og Geology and Geotechnical Engineering, Dept. of Chemistry, Dept. of Applied Chemistry). The Danish soil remediation company AS Bioteknisk Jordrens has the rights of the patent and is developing the method for commercial use.

So far most research has been done on a laboratory scale, where the method has proved to work with different soil and pollution types (3) and (4). Still a lot of work needs to be done in laboratory scale. A research program, where the remediation parameters are found and optimized for different combinations of soil type and heavy metals, is in progress.

A larger outdoor remediation setup called megalab, has been constructed at DTU. The megalab setup is constructed with plane electrode units with an area of about 150 cm^2 placed with a distance of 1 m. The megalab setup is the link between the laboratory scale and full scale remediation. The remediation parameters found in the laboratory are tested and adjusted in the megalab setup before they are adapted to full scale remediation. At present three megalabs tests are running.

A pilot plant treating about 1 m^3 of soil has been constructed and tested at AS Bioteknisk Jordrens. In this pilot plant the electrode units were the same as those that are going to be used in the first full scale electrodialytic soil remediation which will take place in 1998.

RESEARCH PROGRAM. SOIL AND POLLUTION CARACTERIZATION

In soil heavy metals are retended in different ways. The heavy metals can be adsorbed to the solid particles at ion exchange sites by electrostatic forces or the adsorption can invonve chemical bondings. The heavy metals can also precipitate with other dissolved ions.
When an electric current is applied to the soil the ions that are bound in exchange sites will carry a part of the current, and the heavy metals that are bound in these sites are easily removed from the soil. In order to get a succesfull remediation it is necessary to desorb the heavy metals that are adsorbed with chemical bonds and to dissolve the precipitation products that contain heavy metals, too.
An acidification will in most cases mobilize the polluting heavy metals. During an electrodialytic remediation, an acidic front is developing in the direction from the anode to the cathode. The acid is produced from water dissociation at the interface between the anion exchange membrane and the soil (3). Meanwhile there are soils where the pollution is not mobilized by the acid. In a research program soil parameters, heavy metals and heavy metal combinations, are identified for cases where the soil needs addition of a desorbing agent in order to mobilize the heavy metals before or during the electrodialytic remediation process. The problem may be divided into three categories: (I) The heavy metal is present in the soil in its metallic form, (II) the pollution includes different heavy metals with different retention chemistry, or (III) the soil matrix may have characteristics that makes the electrodialytic soil remediation expensive.

Examples from the three categories are: (I) In Hg polluted soils a part of the Hg is often present in its metallic form, (II) soils polluted from wood preservation industry contain Cu, Cr and As and the problem here is that Cu and Cr will be mobilized in the acidic front while As will be immobile under the acidic conditions, and (III) soils may have a to high carbonate content giving the soil a high buffering capacity. This means that the remediation action will be very time consuming because the soil acidification occurs too slowly. In other soils the problem may be that the electric resistance is high (especially sandy soils).

In all three cases it is possible to improve the soil/pollution conditions by adding a desorbing agent to the soil. This means that after identifying the problem a proper desorbing agent must be found. The desorbing agent needs to make the electrodialytic remediation cost effective and at the same time it must not create a new pollution problem in the soil. Below is given an example of a desorbing agent for a polluted soil from category (III).

REMOVING Cu FROM A CALCAREOUS SOIL

Experimental results with electrodialytic remediation of a Danish loamy sand polluted with Cu were reported in (3). The soil had a low carbonate content and was succesfully remediated from 1360 mg Cu/kg dry soil to a level below 40 mg/kg dry soil. This result was obtained with no addition of desorbing agent to the soil.

Two laboratory remediation experiments were made with another Danish Cu-polluted soil. The soil from the two experiments varied slightly in initial Cu concentration but was taken from the same polluted site. The Cu concentration was high, about 20 g Cu/kg dry soil. The soil was sand with a carbonate content of 11%, and the soil pH was initially 7.6. An electrodialytic laboratory cell as the one shown in figure 1 was used for the experiments. The central compartment had an inner diameter of 4 cm and a length of 10 cm.

In the two experiments the soil was pretreated differently and the electrodialytic remediation parameters such as duration and current also varied slightly in the two experiments.

(A) Initial Cu concentration in the soil 20 g/kg dry soil. A soil sample was acidified with 5% (per weight) of 1 M HCl and by this soil pH was decreased from 7.6 til 7.1. The ion-exchange membranes were obtained from Sybron (Ma3475, Mc3470). In the electrode compartments and in the concentration compartments 250 ml 0.01 M $NaNO_3$ with pH adjusted with concentrated HNO_3 to about 2 was circulated (pH was adjusted in the catholyte every morning during the experiment). The mean current in the cell was 6.5 mA and the duration of the experiment was 26 days.

(B) Initial Cu concentration in the soil 17.7 g/kg dry soil. To a soil sample a 2.5 % ammonia solution was added, and this solution was added continuously during the experiment. The ion-exchange membranes were obtained from Ionics (CR67 HMR 412, AR2045 XZL 386). As electrolyte solution 2,5% NH_3 was used. The mean applied current was 8.2 mA. The duration of the experiment was 21 days.

The experiments were stopped after 26 days and 21 days, respectively. The soil was segmented into slices at the end of the experiments. The content of Cu in each slice was measured in dublicated according to Danish standard DS 259. The normalized Cu-concentration profiles in the soil at the end of the two experiments is shown on Figure 2.

From figure 2 experiment (A) it is seen that the copper concentration only has decreased in less than 2 cm of the soil from the anode side. Thus the remediation occurs very slowly. The acidic front needed to mobilize Cu is developing slowly due to the high buffering capacity of the soil. The calcareous part of the soil must be dissolved by the acid before the Cu is mobilized. Only the soil in the slice closest to the anode was acidified during the 26 days of current. The Cu that has been removed from the slice closest to the anode has been transported in the direction of the cathode but it has been immobilized again after less than 2 cm because pH here was to high to have Cu in the mobile form. Therefore the accumulation is seen. If more acid had been added to the soil before the remediation, the result would have been better, but still the calcareous part should have been dissolved, and this means that current would have been wasted in carrying Ca^{2+} ions instead of Cu^{2+} ions out of the soil.

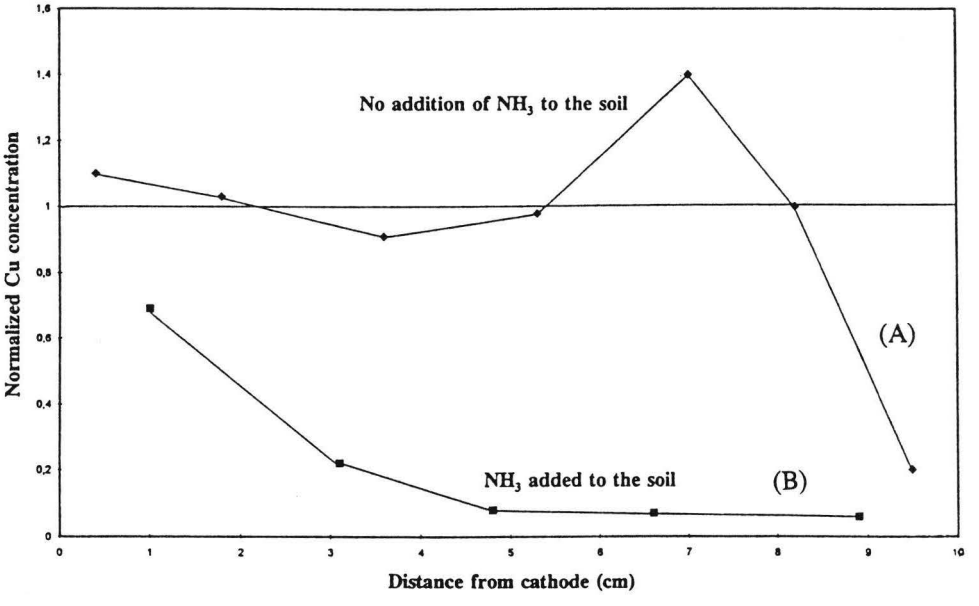

Figure 2: Normalized Cu profiles in the soil in the end of the two experiments.

When ammonia is added to the soil, Cu and ammonia will form $[Cu(NH_3)_4]^{2+}$ complexes. These complexes are charged and will thus be mobile in the applied electric field. When the NH_3 is added to the soil, pH will increase and this means that the calcareous part of the soil will not be dissolved. From Figure 2 experiment (B) it is seen that the addition of NH_3 to the soil improves the remediation compared to the remediation where the acid was added to the soil before the remediation. No accumulation of Cu is seen, because no pH jump is

created. This means that the Cu is transported out of the soil as soon as it is mobilized. The Cu concentration closest to the anode was about 1200 mg Cu/kg dry soil which is a reduction in Cu content of 93 % in this part of the soil. The experiment was stopped before the whole soil volume was remediated, but if current had been passed through the cell for a longer period the copper concentration would have been less than 1200 mg Cu/kg dry soil in the whole soil volume.

The addition of ammonia to the soil resulted in a faster removal of Cu and furthermore also in a decrease in electric resistance in the soil, see Figure 3. This lower resistance is probably due to a higher amount of mobile ions throughout the whole soil volume in the case with ammonia addition. The lower resistance is causing less energy consumption during remediation.

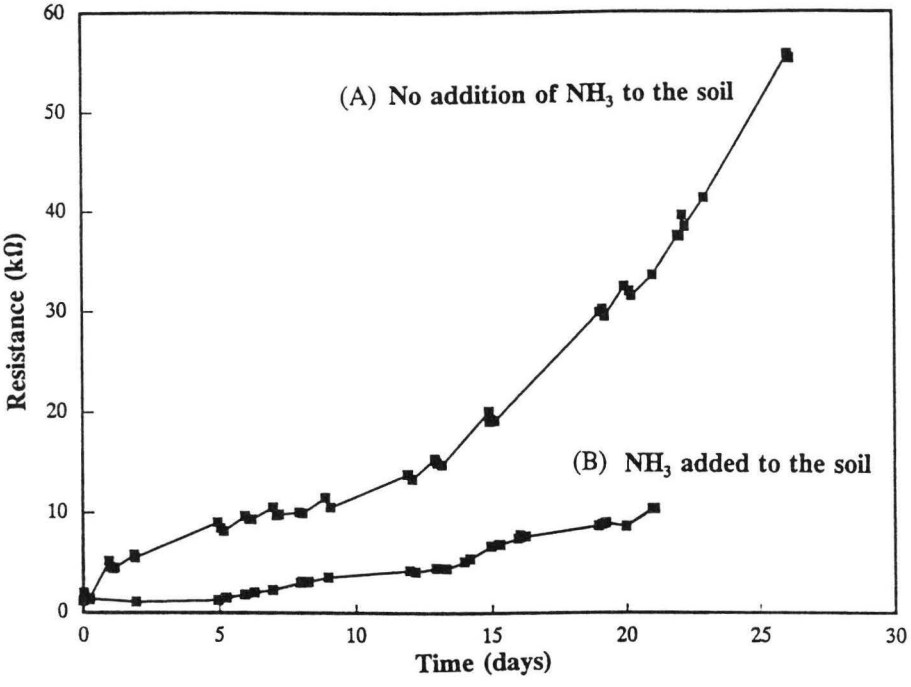

Figure 3: Changes in resistance during the experiments.

From the two experiments described it is demonstrated that an addition of ammonia to the Cu polluted calcareous soil improved the electrodialytic remediation. The copper is transported out from the soil at a higher rate and the calcareous part of the soil is not dissolved. At the same time the remediation is less energy consuming when ammonia is added to the soil.

A megalab test is running with Cu polluted soil from the same site. Ammonia has been added to the soil as it was found to give improved remediation conditions. This test has now been carried out with succes for about a year, see (5). About 800 mg Cu has been removed during the test so far.

FUTURE WORK

The research program where remediation parameters are found for different soil types and pollution combinations will continue at the laboratory scale. An investigation of the quality of the remediated soil will also be made.

A connected research program has been initiated in 1997 where treatment of the heavy metal polluted electrolyte solutions from the remediation process is in focus. This work will continue during the next years.

In 1998/1999 a project on remediation of a sandy loam polluted from wood preservation will be carried out. The pollution is As, Cr and Cu, and remediation of these elements at the same time needs addition of desorbing agent to the soil. The test will be run in megalab scale. The project is financial supported by the Danish EPA.
In the same period another test will be made with a calcareous soil from another wood preservation site. This investigation includes 5 m_3 of soil and will be run in an up-scaled megalab plant.

The first full scale remediation action will be initiated in 1998 at AS Bioteknisk Jordrens. The soil to be remediated is a copper polluted calcareous sand.

ACKNOWLEDGMENTS

AS Bioteknisk Jordrens has demonstrated confidence in the electrodialytic soil remediation method by yielding financial support to the project.

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FLOTATION AS AN ADDITIONAL PROCESS STEP FOR THE WASHING OF SOILS CONTAMINATED WITH HEAVY METALS

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Keywords: chemical treatment, classification, contaminated soil, fine particles, flotation, heavy metals, screening, soil washing, sulfides, zinc

SUMMARY

Conventional soil washing of a zinc-contaminated soil did not lead to an acceptable cleaning result. Flotation experiments were therefore carried out for further cleanup of the fine particle fraction. The removal of the zinc from the fine particle fraction by means of flotation improved the overall soil washing result significantly. The flotation result could be tailored to the cleaning aim of the soil washing process by a proper choice of the flotation parameters. Good cleaning results required a chemical pretreatment of the soil. The results show that an additional flotation step within a soil washing plant could make the soil washing method economically feasible for soils with high contents of fine particles (i.e. clay and silt).

ZUSAMMENFASSUNG

Für einen zinkkontaminierten Boden führte die herkömmliche Bodenwäsche zu unbefriedigenden Reinigungsergebnissen. Zur weiteren Reinigung der Feinkornfraktion wurden deshalb Flotationsversuche durchgeführt. Durch die Entfernung des Zinks aus der Feinkornfraktion mittels Flotation ließ sich das gesamte Reinigungsergebnis bedeutend verbessern. Durch die richtige Wahl der Flotationseinstellung konnte das Flotationsergebnis an das Reinigungsziel des gesamten Bodenwaschprozesses angepaßt werden. Gute Flotationsergebnisse erforderten eine chemische Bodenvorbehandlung. Die Ergebnisse zeigen, daß eine zusätzliche Flotationsstufe in einer Bodenwaschanlage auch für feinkornreiche Böden eine wirtschaftliche Bodenwäsche ermöglichen kann.

RÉSUMÉ

Il etait montré, que le lavage du sol conventionel d´un sol contaminé de zinc, ne menait pas aux résultats de nettoyage acceptables. Pour le nettoyage supplémentaire de la frction de particules fines des essais de flottation étaient fais. L´enlèvement de zinc de la fraction de particules fines par la flottation pouvait notamment améliorer le résultat de nettoyage total. Par le propre choix de l´ajustement de flottation le résultat de flottation pouvait être adapté au but de nettoyage du procé de lavage du sol total. De bons résultats de flottation demandaient une prétraitement chimique du sol. Les résultats montrent, qu´une phase de flottation additionelle dans une installation de lavage du sol peut rendre possible un lavage du sol économique même pour des sols contenants une forte proportion de particules fines.

Contaminated Soil '98, Thomas Telford, London, 1998, 479–490

INTRODUCTION

Soil washing is an established method of cleaning large masses of contaminated soil in a fast and cheap manner. Soil washing can in contrast to biological methods be applied to a wide range of contaminants. In addition, it treats the soil with care in comparison to thermal methods, which favours a subsequent recultivation.
The basic principle of soil washing is the separation of the particles that carry the contaminants from clean particles. Since the contaminants are mainly concentrated - after a wet liberation if necessary - in the fine particle fraction the soil cleaning can be accomplished by classification of the soil by means of sieves and hydrocyclones. Problems occur when too many contaminants are fixed to the coarse fraction or when the proportion of fine particles (i.e. silt and clay) exceeds a certain limit [1,2]. In these latter cases additional process steps must be included to reduce the contaminant concentration of the cleaned fraction, and to enlarge the quantity of cleaned soil by concentrating the contaminants in a smaller fraction, respectively.
Flotation allows to selectively separate particles with different surface properties from each other by introducing air bubbles into the liquid/solid suspension. Hydrophobic particles are caught by the air bubbles and carried to the top of the suspension, whereas hydrophilic particles remain in the pulp. The method requires flotation agents that selectively affect the surface properties of the particles. "Collectors" are used to reduce the wettability of those particles that are to be flotated, whereas "depressants" are to produce or enhance, respectively, the hydrophilia of the particles that are to stay in the suspension. "Frothers" are used to produce a stable froth with which the flotated particles are removed, on top of the suspension [3]. Great experience with different flotation agents for the flotation of metals has been gained in the field of ore processing [3,4]. It seems reasonable to utilize this experience for the cleaning of heavy metal-contaminated soils. As an additional process unit in a soil washing process a flotation step could reduce the mass of fine particles that has to be disposed. However, the application of flotation for the treatment of the fine particle fraction will only be successful if the contaminants are not spread homogeneously over all fine particles, but if clean fine particles exist in the soil along with contaminated ones [5].

The goal of the present work was to determine whether flotation can improve the cleaning efficiency of soil washing processes for a given heavy metal-contaminated soil and to investigate the effect of different flotation agents on the cleaning result of a flotation step.

MATERIALS AND METHODS

Characterisation of the soil material used

The investigations were carried out with a zinc-contaminated soil material that was excavated from a former industrial site. The soil material is characterized by a sand fraction (i.e. 50 - 2,000 µm) of about 80-mass% and a clay fraction (i.e. < 2 µm) of over 10-mass%. The particle size distribution was determined by wet test sieving of a soil sample of about 200 g. The fraction >2 mm was less than 0.1 mass-% and thus ignored. Measurements with a laser particle sizer (Sympatec Helos with a lense of 100 mm focus

length) were carried out for a higher resolution in the finest particle size range (<100 µm).

The zinc concentrations in the size fractions obtained by sieving of the soil sample were determined by extraction with HNO_3/H_2O_2 according to the German Standard DIN 38414 T7 and measuring the zinc concentration in the extract with a Perkin Elmer 2000 OES with ICP according to DIN 38406 T22. The average zinc concentration was 3,200 mg/kg dry matter (d.m.).

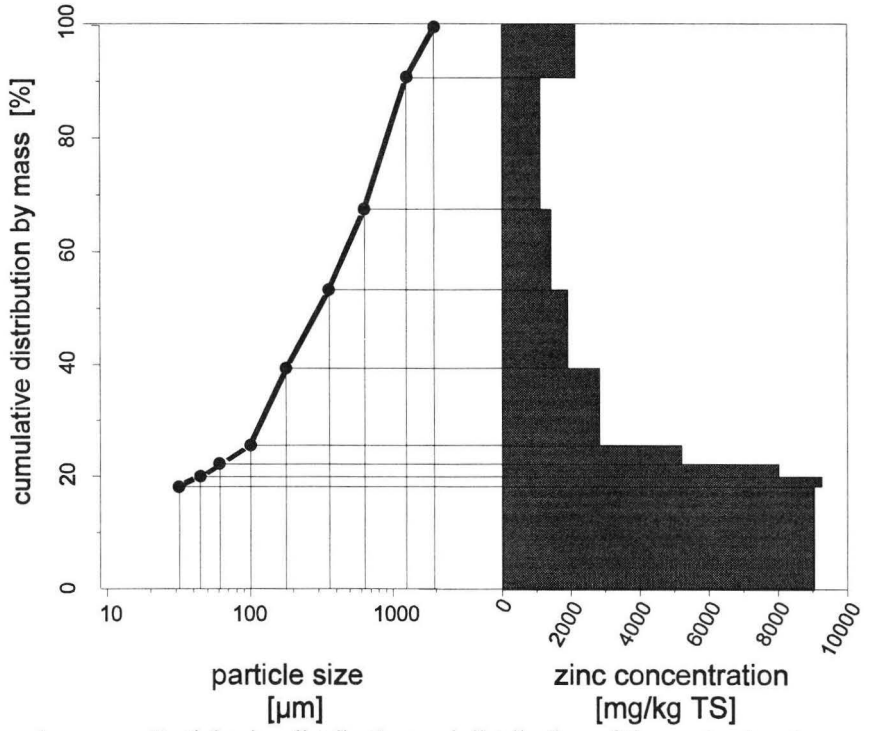

Figure 1. Particle size distribution and distribution of the contaminants over the particle size

Figure 1 displays the particle size distribution and the zinc concentrations in the particle size fractions. In the right-hand part of the figure the fractional part of the total mass of the contaminant is represented by the area of the respective rectangle. The figure shows that the zinc concentration increases with decreasing particle size. There is, however, a significant zinc concentration in the fractions of coarser particles, too. Thus, a sufficent soil cleaning would not be achieved by classification only.

Since most of the flotation agents - especially collectors - do not have an effect on chemical elements in general, but on special chemical compounds (e.g. metal sulfides), a further knowledge about the chemical form of the metal contaminants is useful to find suitable flotation agents. Therefore a chemical extraction of the zinc with the method suggested by Förstner and Calmano [6] was carried out, by which the zinc present in the soil is extracted in sequential steps with different solvents and in different extraction

milieus (pH-value, temperature, solvent, duration). The analysis of the zinc contents in the different extracts indicate that different chemical compounds of the zinc were present in the soil (Table 1). Thus a single collector will probably not be sufficient for an extensive removal of the zinc from the soil by flotation.

Table 1: Chemical compounds of the zinc in the soil found by sequential extraction after Förstner and Calmano [6]

	zinc is	% of total zinc
I	exchangeable	12,8 %
II	carbonatic	32,5 %
III	easily reduceable	51,5 %
IV	moderately reduceable	1,7 %
V	sulfidic / organic	0,8 %
VI	in residual fraction	0,6 %

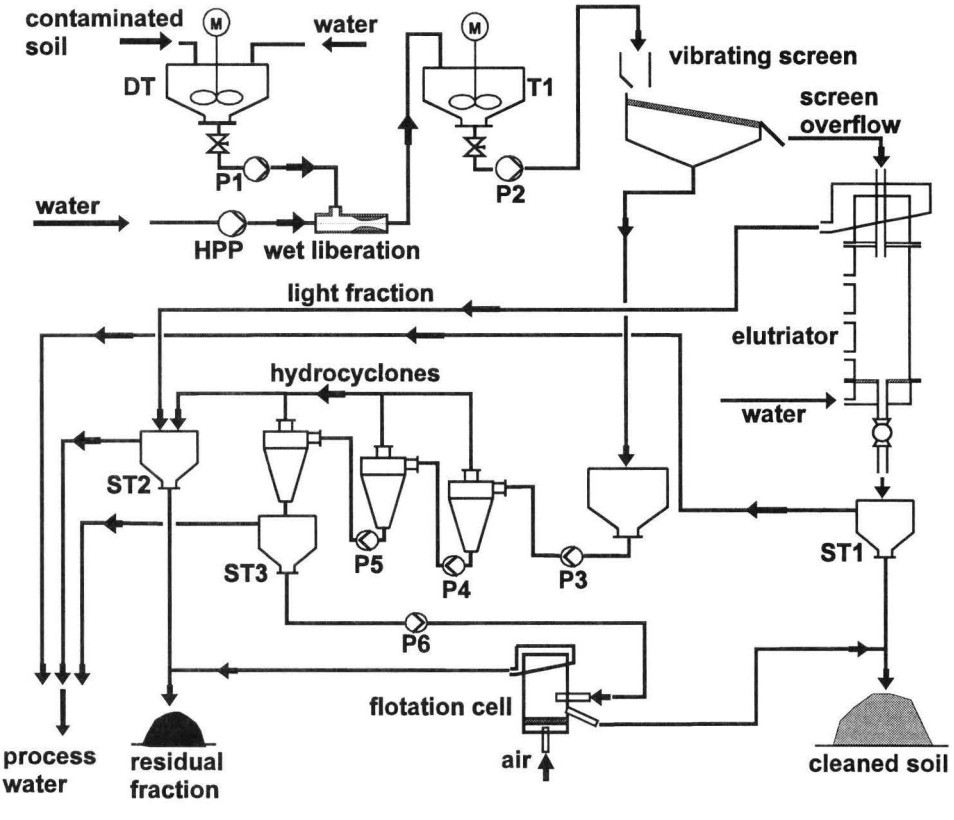

Figure 2. Soil washing test plant at Technical University Hamburg-Harburg (DT: dispersing tank; HPP: high pressure pump; P1 - P6: pumps; T1, T2: tanks; ST1, ST2, ST3: sedimentation tanks)

The flotation experiments were carried out batchwise with a laboratory-scale flotation cell with a volume of 350 ml (Figure 3). For each experiment a soil mass of 50 g was suspended with about 250 ml water in a glass beaker. If the soil sample was intended to be chemically pretreated the pretreating agents were added into this suspension. According to a method to clean harbor sediments which is described by Eberius [7] two different methods of chemical pretreatment were applied, namely the hydroxilation and the sulfidation. The hydroxilation was done by adding a mixture of NaOH and Na_2CO_3 with a ratio of 2:1 moles and shaking it for about 14 hours before the flotation experiment. Sulfidation was carried out by adding a Na_2S-solution only half an hour before the flotation experiment in order to avoid a complete oxidation of the sulfides. The goal of pretreating the soil was to achieve a uniform chemical bonding of the zinc. A uniform chemical bonding might then allow better flotation with the suitable agent.

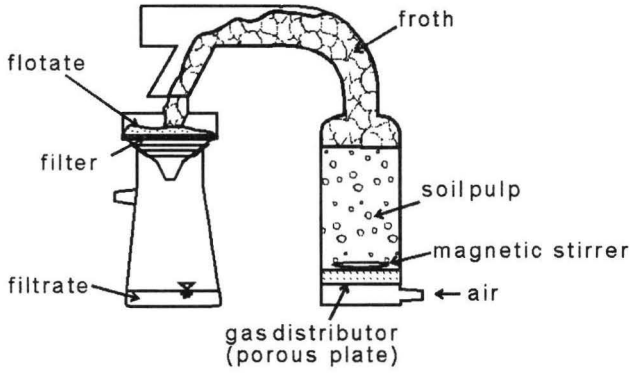

Figure 3. Laboratory-scale flotation cell

A screening of different flotation agents with specific effects on different chemical bounds of heavy metals was carried out. The soil material was conditioned with the flotation agents in the glass beaker for half an hour before the flotation experiment and continuously stirred. The types and trading names of the flotation agents used are listed in Table 2. The agents were applied in different combinations and concentrations.
The pH level was adjusted by adding either NaOH or NaCl. The conditioned pulp was then poured into the flotation cell. Water was added to fill the cell up to a volume of 350 ml. The flotation air was supplied through a porous glass plate with a pore diameter of about 60 µm at a feed rate of 50 or 130 $l\,h^{-1}$, respectively. The air supply was turned on before filling in the soil suspension in order to avoid clogging of the pores of the gas distributor by the soil particles. The suspension in the flotation cell was stirred with a magnetic stirrer. The produced froth was collected on a filter funnel (filter paper Schleicher & Schuell, porosity class "blue") to dewater the flotated solids. The air supply was maintained as long as soil particles were entrained in the froth. After each flotation experiment the solids that remained in the pulp were filtered, too. Both fractions were dried in a drying oven and then weighed. The zinc concentrations were determined as described above.

Table 2: Flotation agents used

		trading name	chemical description
frothers[1]:		Flotanol C7	alkyl polyglycole
		Flotanol D14	alkyl polyglycole
		Talloel	carboxylic acids
			sodium dodecyl sulfate (SDS)
collectors:	for sulfide flotation	Xanthate	potassium hexyl xanthate (KHX)
		Hostaflot LIB	dithiophosphate
	for flotation of oxides	Flotigam OA	oleylamine acetate
		Flotinor AT	sodium alkane sulfonate
	for organic matter		rape seed oil
depressant:		Tylose	technical methyl cellulose

[1]) Frothers often have collecting characteristics, too.
all agents were supplied by Hoechst AG

Separation performance parameters

The separation results achieved by flotation are described with the solids removal β_S, the zinc removal β_{zn}, and the decontamination ratio r_d. The solids removal β_S is the portion of the solids in the pulp that is entrained into the flotate fraction:

$$\beta_S = \frac{m_{fl}}{m_f} \tag{1}$$

where m_{fl} denotes the solids mass in the flotate, and m_f is the solids mass initially present in the soil pulp. The zinc removal β_{zn} is defined in the respective way:

$$\beta_{zn} = \frac{m_{zn,fl}}{m_{zn,f}} \tag{2}$$

where $m_{Zn,fl}$ denotes the zinc mass in the flotate and $m_{Zn,f}$ the zinc mass in the feed soil pulp.

The difference between the zinc concentration of the feed material and that of the cleaned tailings is described by the decontamination ratio r_d, which is defined by

$$r_d = \frac{c_f - c_t}{c_f} \tag{3}$$

in which c_t denotes the heavy-metal concentration in the tailings fraction. A cleaning of the soil material and an enrichment of the heavy metal in the flotate is indicated by $r_d > 0$. The decontamination ratio r_d should approach the theoretical maximum of $r_d = 1$ as close as possible.

RESULTS AND DISCUSSION

Soil washing process without a flotation step

Figure 4 shows the mass balance of the soil for each single step of the soil washing that was carried out in the test plant (Figure 2). After liberating and sieving the material, which had an initial zinc concentration of 3,200 mg/kg d.m., the remaining zinc concentration of the sieve oversize material was only 379 mg/kg d.m.. Thus this material was reusable for some construction purpose according to the limit LAGA Z2 of 1.500 mg/kg d.m. that is presently applied by many German authorities.

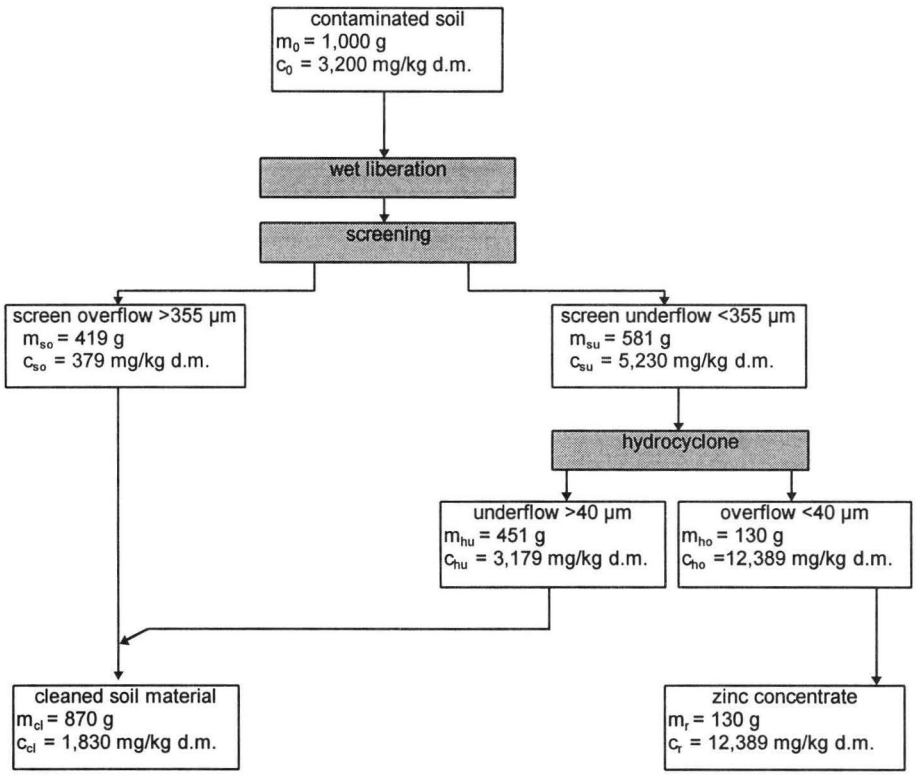

Figure 4. Mass balance of the soil cleaned in the soil washing process without flotation step (note that this process leads to a residual zinc contamination in the "cleaned soil material" of 1,830 mg/(kg d.m.) which exceeds the limiting value LAGA Z2 of 1,500 mg/(kg d.m.)

The light soil portion of the sieve oversize fraction that was discharged on top of the elutriator was negligible and therefore not considered in the mass balance in Figure 4. Thus a cleaned fraction with a remaining zinc concentration of only 379 mg/kg d.m. can be obtained just by sieving of the soil material. This cleaned fraction, however,

consists of 41.9 mass-% of the original soil mass only. By subsequent hydrocyclone separation of the sieve underflow a mass of 45.1% of the initial soil mass was discharged in the underflow fraction of the hydrocyclone. By adding the hydrocyclone underflow to the cleaned sieve oversize material a cleaned fraction of 87 mass-% of the soil mass fed into the entire process was achieved. Furthermore the hydrocyclone separation brought about a reduction of the zinc concentration from 5,230 mg/kg d.m. down to 3,179 mg/kg d.m. in the hydrocyclone underflow (Figure 4). This cleanup of the sieve underflow by means of hydrocyclone separation, however, was not sufficient as it led to a residual zinc concentration of the cleaned material of 1,830 mg/kg d.m. which was too high for a reuse according to the LAGA Z2-limit of 1,500 mg/kg d.m.. Therefore it is not possible to enlarge the mass yield of the cleaned material by adding the hydrocyclone underflow to the clean sieve overflow fraction.

The results of the flotation experiments carried out for further cleanup of the hydrocyclone underflow are plotted in Figure 5. Each dot marks the result of a single flotation experiment with the solids removal β_s to be read off the abscissa and the decontamination ratio r_d to be read off the ordinate. Since the solids removal β_s means a loss of reusable material, its value should be as small as possible in order to keep the mass of the reusable material large, whereas in order to achieve a low residual zinc concentration the decontamination ratio should be as high as possible.

As Figure 5 shows, most of the experiments carried out without a hydroxilation or sulfidization pretreatment did not lead to satisfying cleaning results. High decontamination ratios occurred in conjunction with a high solid removal and vice versa. The best cleaning result - marked by an asterisk in Figure 5 - was gained by a very acidic flotation regime with a pH-value below 4, which led to a large chemical extraction of the zinc. Since it was the aim of this work to investigate flotation as a means of cleaning heavy metal-contaminated soils by removing the contaminants without dissolving them, the cleaning mechanism of dissolving the heavy metal into water cannot be seen in any connection to the other experiments that are presented in this paper.

The reason for these unsatisfying results for flotation without chemical soil pretreatment might be that the zinc is not present in the soil in one particular chemical form like it is in an ore, but in different chemical compounds, as was found by the sequential extraction (see above).

The results gained with soil samples that were chemically pretreated in order to make the chemical bonds of the zinc uniform bear this assumption out. Figure 5 shows that chemical pretreatment can improve the flotation result significantly. By sulfidation or hydroxilation prior to flotation of the soil, a higher decontamination ratio - and thus a lower zinc concentration in the cleaned tailings - can be achieved with the same solids removal, or the same decontamination ratio may be obtained with a smaller solids removal in the flotate, respectively. If, for example, a decontamination ratio r_d of 0.5 is required, 30 mass-% of the feed mass had to be removed in the flotate if the soil material had not been pretreated. Sulfidation can reduce the mass fraction that has to be removed down to 10 mass-%.

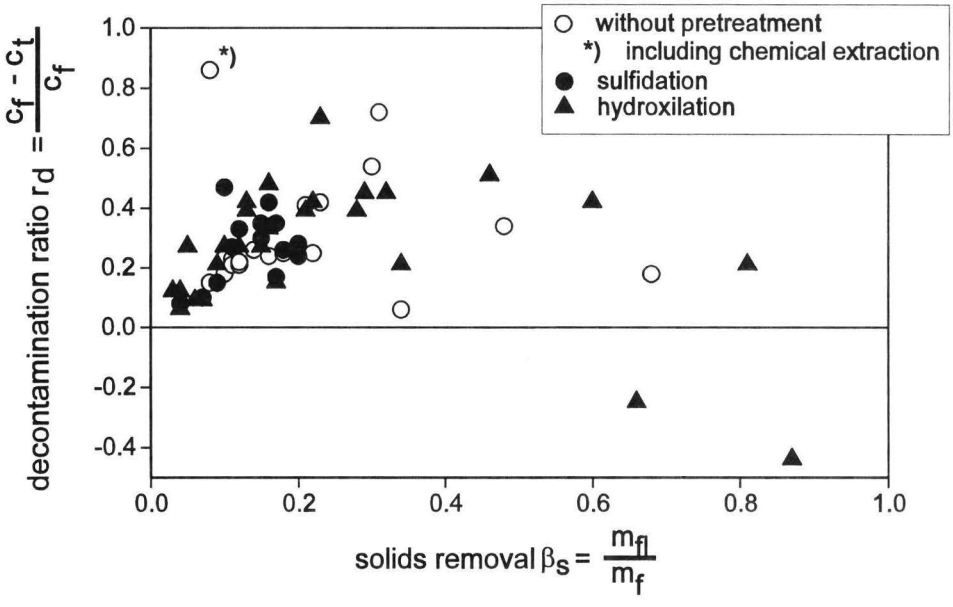

Figure 5. Flotation results with and without chemical pretreatment

Integration of a flotation step in a soil washing process

The basic question is whether a flotation step within a soil washing process can improve the overall cleaning result to such an extent that soil flotation becomes economically feasible. The integration of a flotation step into a soil washing plant will be demonstrated using data from test runs with the soil washing test plant (shown in Figure 2). The decontamination ratio r_d that must be achieved in the flotation step for the cleaned soil to fulfill the requirements of the LAGA Z2 limit may be obtained from mass balances for the flotation and for the soil washing process as a whole.

$$r_d \overset{!}{\geq} 1 - \frac{c^*}{c_{hu}} - \frac{m_{so} \cdot (c^* - c_{so})}{m_{hu} \cdot c_{hu}} \cdot \frac{1}{1 - \beta_s} \qquad (4)$$

Equation 4 provides a relationship between the minimum decontamination ratio r_d and the solids removal β_s depending on the upper zinc concentration limit c^* of the over-all cleaned fraction, the zinc concentrations in the hydrocyclone underflow c_{hu} and the sieve overflow c_{so}, and the solids masses of the hydrocyclone underflow m_{hu} and the sieve overflow m_{so}, respectively.

The boundary indicated by Equation 4 together with the experimental results shown in Figure 5 has been plotted in Figure 6. Experimental points above the curve indicate operating conditions in the flotation step which will lead to zinc concentrations c_{cl} in the cleaned soil below the LAGA Z2 limit. Among these "good" flotation results is the optimum that one, which shows the smallest soil removal and thus the largest yield of

cleaned material. This flotation result is marked in the diagram with "1)". It was achieved by hydroxilation with 5,000 mg/kg d.m. of the 2:1-$NaOH/Na_2CO_3$ solution and subsequent conditioning with 400 mg/kg d.m. oleyl amine acetate, 500 mg/kg d.m. potassium hexyl xanthate, 400 mg/kg d.m. Talloel and 200 mg/kg d.m. Tylose at a pH value of 10.5.

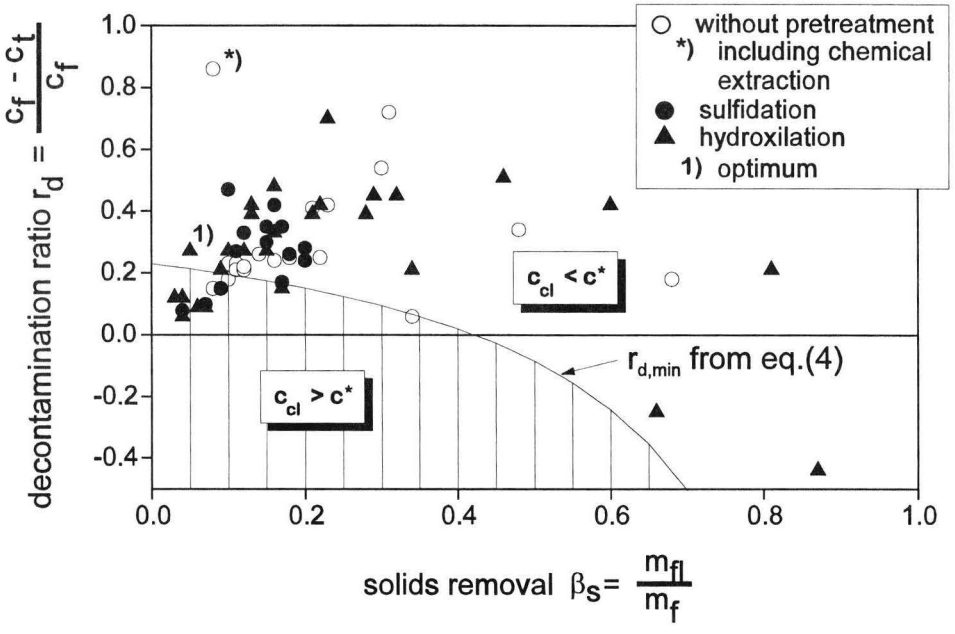

Figure 6. Determination of optimum flotation conditions

The mass balance of the soil washing test with integration of the flotation step under these conditions is shown in Figure 7. Due to the high selectivity of the flotation by which a small mass with a zinc concentration of 20,322 mg/kg d.m. was extracted from the hydrocyclone underflow, the zinc concentration of the hydrocyclone underflow was reduced from 3,179 mg/kg d.m. down to 2,258 mg/kg d.m. in the tailings fraction. After adding the latter to the sieve overflow, the resulting clean fraction had a zinc concentration of only 1,328 mg/mg d.m. and is therefore reusable according to the LAGA Z2-value of 1,500 mg/kg d.m. This example shows, that the process can be tailored to achieve results close to the concentration limit by choosing a proper flotation adjustment with the objective of yielding a reusable mass that is as large as possible.

Without a flotation step to clean the hydrocyclone underflow, a process arrangement that brought about a clean and reusable soil fraction consisted of sieving only. This process arrangement, however, led to a mass yield of only 41.9 mass-% of the original mass. In comparison to this conventional soil washing process the integration of a flotation step led to a soil mass yield of 84.7 mass-% and thus to an increase in the reusable soil mass of over 50 %.

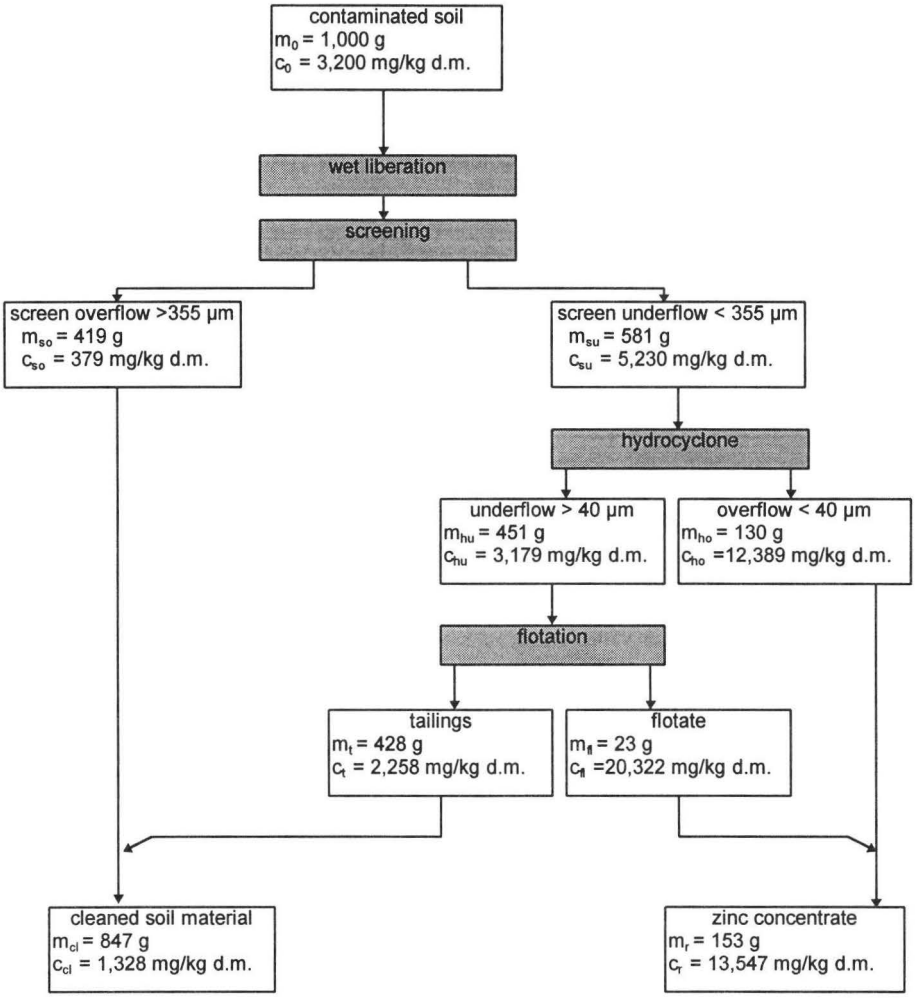

Figure 7. Mass balance of the solids and the zinc over the entire soil washing process including a flotation step (operating conditions see text).

CONCLUSIONS

A selective removal of zinc-contaminated soil particles from the fines fraction can be achieved by flotation. A chemical pretreatment helps to enhance the selectivity of the process. The optimum flotation environment must be found out by experiments carried out with the respective contaminated soil. The present example has shown that the integration of a flotation step in a conventional soil washing process can remarkably improve the cleaning result of a zinc-contaminated soil by either increasing the mass yield of reusable soil material or reducing its residual zinc concentration. Since the effect of the flotation is the further clean-up of the fine particle fraction, flotation might

also help to clean soils with high contents of fines that can not be cleaned economically with conventional soil washing processes at present.

SYMBOLS

c	[mg/kg d.m.]	zinc concentration
c*	[mg/kg d.m.]	limit value of the zinc concentration
m	[g]	solids mass
m_{zn}	[g]	zinc mass
r_d	[-]	decontamination ratio, def. by Equation 3

Greek symbols

β_{zn}	[-]	zinc removal, def. by Equation 2
β_s	[-]	solids removal, def. by Equation 1

Subscripts

0	untreated soil
cl	cleaned fraction
f	feed
fl	flotate
ho / hu	hydrocyclone overflow / underflow
r	highly contaminated residual fraction
s	solids
so / su	sieve overflow / underflow
t	tailings

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INTELLIGENT SOIL
A DIFFERENT APPROACH TO SOIL?

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KEYWORDS:
intelligent soil, soil properties, contaminated sites, reactor, remediation concept, characterisation, natural attenuation

SUMMARY:
What makes soil so interesting and why is bioremediation of the soil becoming increasingly popular? The soil would appear to be a lifeless heap of sand, mud and stones, on which you can build houses, grow grass or wheat or lay a road. However, appearances can be deceptive.

Contaminated Soil '98, Thomas Telford, London, 1998, 491–494

What makes soil so interesting and why is bioremediation of the soil becoming increasingly popular? The soil would appear to be a lifeless heap of sand, mud and stones, on which you can build houses, grow grass or wheat or lay a road. However, appearances can be deceptive.

Upon closer examination, we discover that the soil contains a wealth of information. Information which enables the soil to change and adapt to new conditions, for example. Just think of the huge amount of DNA stored in the microorganisms in the soil, sometimes up to a depth of several kilometres. This genetic information contains the bleuprints for the tools, i.e. the enzymes, which catalyse countless chemical reactions and which help make the soil what it really is: a complex combination of physical, chemical and biological factors in continuous and dynamic interaction. The definition of soil given in Webster's dictionary is interesting in this context: "the upper part of the earth crust consisting of organic and inorganic material, water, air and micro-organisms that together form a biological entity".

For years, it has become fashionable to consider the soil as a reactor vessel in which biological degradation reactions occur, which can be controlled just like in a real reactor. In this mechanistic model it is assumed that the soil can be manipulated and understood, and that if we do enough research we will eventually be able to direct and predict the processes in the soil. Under this approach, the heterogeneous nature of the soil is a problem which makes life difficult for engineers.

In real life, the soil and what happens in it are much more complex and less easily understood than perhaps we would like. If you look at it like this, there are actually many similarities with the weather. Scientists can investigate and study it a great deal, but the system is so complex that it is difficult, and perhaps even impossible, to fully understand and predict, let alone control, however powerful the computers and sophisticated the models used have become.

Nevertheless, in many fields, such as the weather or the economy, we are perfectly capable of dealing with uncertainties. In industry, important decisions are taken every day on the basis of the dollar rate or economic variables which nobody can predict. As far as the soil is concerned, perhaps we still have to discover that you cannot eliminate all uncertainty, that some things will always be beyond our grasp, however much research we do. The system is simply too complex.

In the soil, formation and degradation reactions constantly follow one another in natural cycles. Changes (mutations) in the genetic material continuously modify and improve the biological tools, which means that after some time even unexpected chemical contamination can be degraded. Microbiologists call this adaptation. It could also be referred to as the soil's ability to learn, or to organise itself. Substances such as perchloroethene and trichloroethene, which initially hardly break down, are eventually degraded more and more without human intervention. In other words, the soil is not passive, rather it is responsive.

Instead of viewing the soil as an inanimate reactor, we could consider it as a complex and dynamic system, with the ability to organise itself, to learn and to clean itself. In short, we could consider it to be an intelligent organism. This creates a quite different, more positive, image of the soil. The soil gets an identity, and is not as helpless as we always thought it was.

Of course, sceptics could argue that this might encourage us not to worry about it, to use this self-cleaning ability as an excuse to go on polluting. The soil will fix itself, don't worry about it. However, it might well be the other way round. The soil as a living organism confronts us with its beauty and uniqueness and demands respect. Furthermore, something which is alive can die, so protection against outside threats is important.

Besides threats there are also opportunities. The solutions to soil contamination are already in the soil and its ability to adapt. In other words, the soil has a great capacity to learn and regulate itself. Under this approach, heterogeneity is not a troublesome complication, but an essential aspect of the soil. This is because it is the heterogeneity of the soil which leads to greater complexity and more path-ways, and therefore more opportunities, for certain degradation and detoxification processes to start.

Contamination entering the soil, for example oil from a leaking tank, could be considered as an external stimulus which the soil responds to in order to maintain a dynamic equilibrium. And it has a memory. The next time the stimulus occurs the soil will react more quickly. It is as if the soil becomes smarter.

A good example of this is provided by potato eelworm, a nematode, which is treated by injecting 1,3-dichloropropene into the soil. The more often the soil is treated with the pesticide the more quickly it is degraded. This means that farmers have to use it more often, and in higher doses. This can be demonstrated by degradation tests, which in fact serve as a kind of IQ test.

The soil is adapting constantly and is therefore developing all the time. This development is influenced by a range of factors, such as the climate, vegetation and use by humans or animals. Contamination is a factor which can have a major effect on the development of the soil and, if serious, it may threaten the life and balance of the soil. However, most contamination spontaneously leads to recovery reactions, in the same way as our bodies respond to infections.

This results in recovery, accompanied by an irreversible development. The soil has changed and has learnt something, it has built up resistance, and the next time it can respond more quickly. Just like a body which can recognise the return of an earlier infection and can prevent illness through a specific, learnt response.

What are the consequences of taking this different view of the soil? It suggests that the soil is partly beyond our comprehension, but also that it is highly creative, that it can look after itself and holds many promises. Soil with some human characteristics. It is interesting to determine to what extent this view of the soil could influence the policy, technical and remediation aspects of soil pollution, and to what extent it can open up the way to an entirely new way of dealing with the soil.

NORTH EDINBURGH PROJECT

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Keywords: Contaminated sites, oil products, gasworks, authorities' role, behaviour of contaminants, risk, sustainability, decontamination techniques, geophysical methods, bioremediation.

SUMMARY

The North Edinburgh Project is of strategic importance to the City of Edinburgh Council. The aim of this £62M project is to secure 3,000-4,000 additional jobs for the City in an area where unemployment and social deprivation are major disadvantages. It proposes to bring back into use a large area of land, contaminated from past industrial use, that lies between the community and the Waterfront for the benefit of the City as a whole. It is a complex project involving public and private sector funding and to deal with the demands of such a complex project, a variety of innovative solutions have been adopted to evaluate and assess risk, and to involve the community at the same time.

Contaminated Soil '98, Thomas Telford, London, 1998, 495–511

INTRODUCTION

If you asked a resident what he or she regarded as the Waterfront of the City, the answer would invariably be Leith. This reflects the success of the Leith Project, begun in 1981 as a joint project between the local authorities and the Scottish Development Agency. Today the industrial decline of Leith has been arrested and a platform of confidence created particularly in the housing sector. Recent developments such as the relocation of The Scottish Office to Victoria Quay and the proposed Ocean Terminal, in the Western Docks, all point to Leith having an assured future within the City's development and property market. Despite the successful reintegration of the historic core of Leith into the City, Leith is only a small part of the City's Waterfront.

STRATEGIC APPROACH

In development terms the City is one of the few cities in the UK where physical development is matched by a growth in population. Its economic success is because it has adapted to changing economic circumstances but its future prosperity will depend on its continued ability to change and grow in an environmentally sustainable way. The Waterfront has a key role in the further growth of the City (Figure 1):

- It contains more than half of the City's derelict and vacant land. This must be used to avoid further pressure on greenfield land and promote sustainable development.
- The North Edinburgh area contains some of the greatest concentrations of unemployment and disadvantage within the City. A means must be found of promoting development to alleviate these problems.
- Improved transport links to the City Centre can make the area highly accessible.
- The special Waterfront character and the potential for major improvement can form a key attraction for development.

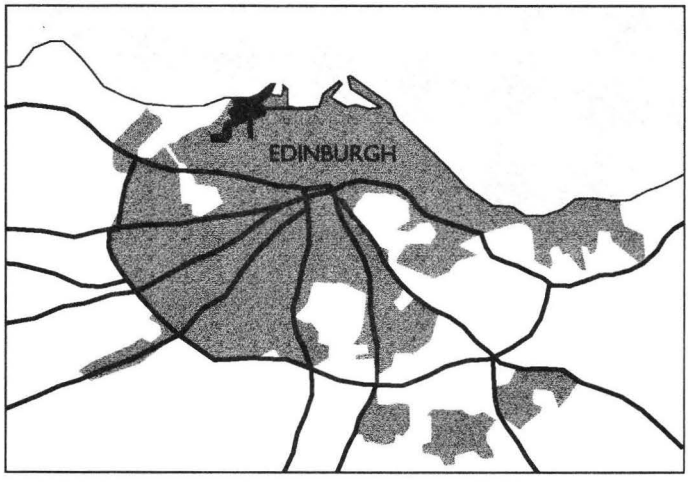

Figure 1
North Edinburgh Project and City's Waterfront

WATERFRONT VISION

In 1995 and 1996, consultants EDAW carried out a major study of the Waterfront on behalf of the Local Enterprise Company, Lothian and Edinburgh Enterprise Limited, (LEEL). The study, titled "Regaining the City's Edge: the Waterfront Challenge." concluded that the Waterfront was not fulfilling its potential, the area was perceived as remote and difficult to access and with a poor environment and image. When development was occurring it was not sufficiently benefiting areas like Granton, Pilton and Muirhouse (Photograph 1) with their social problems and lack of employment opportunities. The study proposed a number of goals for attracting development - improving access, improving the environment, creating new housing and access to employment, leisure and community facilities. The City of Edinburgh Council adopted the vision behind these goals on 15 January 1997.

Photograph 1
The Waterfront at Granton

CHALLENGE FUNDING SUCCESS

That decision was the catalyst for The City of Edinburgh Council (the Council), together with LEEL, Scottish Homes, and the private sector to put together a major project that will deliver the vision. The North Edinburgh Project, concentrates on the western end of the Waterfront and will cost £62.0M to implement. Through a competitive process, the Council secured an award of £7.0M of Central Challenge Funding from the Government on 5 March 1997, which has given the principal public sector partners, the Council and LEEL, the confidence to confirm their funding commitments of £10.5M and £10.0M respectively. The project timescale set by the Challenge Funding award is three years, from April 1997 to March 2000. The high levels of public sector investment is to help secure private sector confidence and will be spent on the following actions to provide a platform for regeneration and further development (Figure 2):

- Acquisition of major derelict and vacant sites.
- Rehabilitation of contaminated land.
- New road links from Ferry Road and the strategic road network.
- Access into the key sites.
- Site infrastructure for development.
- Cycleways and green corridors.
- Helping with major housing renewal at Central Muirhouse and West Granton.
- Refurbishment of Muirhouse Shopping Centre.

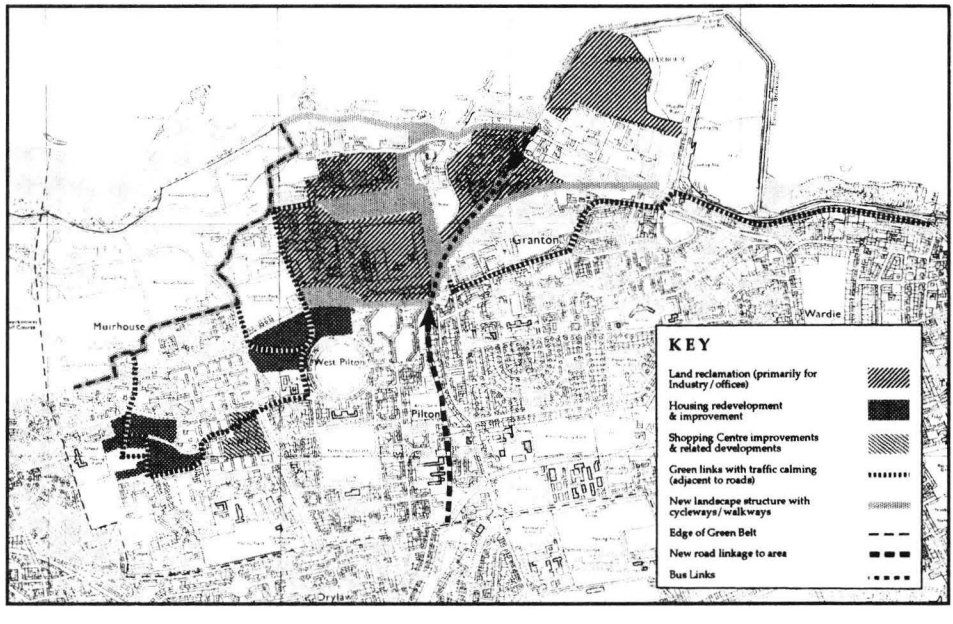

Figure 2
Plan of the Challenge Funded North Edinburgh Project

AUTHORITIES' ROLES

To deliver this major project the partners agreed what their respective roles in the North Edinburgh Project would be:

- The Council will assemble the derelict and vacant land and invest in infrastructure;
- LEEL will undertake land reclamation/decontamination and environmental improvements under their statutory powers;
- Scottish Homes and the Council will undertake the major housing renewal;
- The Council with LEEL and Boland Scottish Properties will undertake the refurbishment of Muirhouse Shopping Centre,

COMMUNITY PARTICIPATION

The local community tempered their "cautious welcome" of the North Edinburgh Project with a degree of scepticism about elements of the action plan. The Council decided to involve the community and held a seminar on 11 May 1997. Following a presentation, the community representatives divided into five workshop groups to discuss what they had heard. In doing so they were asked to consider future land use patterns and ideas for a city park. Their desire is to become a "real partner" in the process through regular meetings with the Council, co-ordinated by the community and held locally. They also expressed a need for plans that can be understood, and an opportunity to visit other communities involved in similar developments. Their concerns included "how will the land be decontaminated, what impact will the development ultimately have on overall pollution levels and therefore health, what green areas/spaces will there be and the proposed land use pattern?"

The involvement of the community on an ongoing basis is vital to the success of the project. Through the umbrella of the Pilton Partnership, further local meetings have been held on sensitive issues such as the new road link from Ferry Road. Information on progress has been published in the local newspaper and a video has been produced on the aims of the project. Continued dialogue with the community can not only assist in overcoming its scepticism but will make the Council's progress more transparent and accountable.

FUNDING STRATEGY

Given that substantial lead-in time is needed to investigate the nature of the contaminated land, a funding strategy was agreed that invests in major housing renewals and the shopping centre refurbishment in year 1, followed by a start to decontamination in year 2 and construction of the new access road in year 3. This targets public sector funding at the more expensive elements, the decontamination and the access road, in years 2 and 3 and also enables private sector funding to be levered into these years for the housing/shopping centre elements, following a first year public investment in preparatory works.

A LONG TERM PLANNING VISION

Having accepted the strategic economic argument for investing substantial resources, the Council and LEEL wanted assurance from a long term planning vision that the maximum benefits are being gained. Such a planning vision could guide investment and should be innovative, yet soundly based on the property market and the aspirations of the local and wider communities.

Selected consultants with an international reputation in urban design tendered for the study. It is in two parts. It will firstly review and analyse all existing proposals, studies and ideas to produce a strategic long term vision for the Granton to Leith area. The second part of the study will be to prepare a detailed and practical development concept of the Granton area, establishing the optimum property market development mix, the direct and indirect economic, social and community benefits and from that to develop a financial model with a cashflow analysis. To ensure the participation of the community, workshops will be held during study preparation. The timescale for completion is April 1998. It will be used by LEEL to secure Board approval to invest precise sums in individual projects. It will also form the basis of an alteration to the Council's approved North West Local Plan and will assist in formulating new planning policies for the area.

PROJECT MANAGEMENT

To deliver the project actions by March 2000, the Council has set up a Special Projects team in the City Development Department to focus on delivery of the project. A partnership agreement with LEEL, similar to the Leith Project, will be entered into defining roles and responsibilities of the Council and LEEL. The team will lead the project and co-ordinate all jointly funded activity in the Challenge Funded package. This arrangement could evolve in the future into some form of special joint development vehicle depending on the conclusions of the economic impact study.

DECONTAMINATION TASK

Few people appreciate the scale of task to decontaminate the derelict land at Granton because the area is not accessible to the public. The Granton Gasworks and Texaco/Shell oil depots are either hidden behind security fences or from the public road by other industrial buildings. The area of the Granton Gasworks alone is larger than the Georgian New Town in the City Centre. The process of establishing the degree of contamination and risk began on two fronts, firstly by the Council and LEEL for the Texaco/Shell oil depots and secondly on the Gasworks by British Gas Properties plc undertaking their own development study in parallel.

TEXACO/SHELL OIL DEPOTS

The Texaco site was first occupied by a timber yard and small gasworks in 1893. In the 1930s Texaco developed a fuel oil depot which was further developed in the 1960s into an oil terminal for storage and handling of gas oils, fuel oils and motor spirits. There was no processing on site. By 1987, the 15 storage tanks, structures, compounds and buildings were dismantled to ground level. There is little visual evidence of past use. Before the Shell site became a petroleum store in 1912, it was a cricket ground. In 1914 it was occupied by eight storage tanks to which was added two further tanks in 1964. A year later the terminal was redeveloped and in 1975 a totally different layout of 10 storage tanks was developed, followed by a further storage tank in 1977. In 1987 the storage tanks were dismantled and buildings removed and in 1988/89, the bulk of contaminated made ground removed.

STAGE 1 FINDINGS

Oil product contaminated water was apparent and an orange coloured silt material lay in a water issue on Texaco. The previous reports on this site prepared by Texaco's consultants, concluded that there was little contamination on site and assumed that the stiff sandy grey clay stops contamination from going deeper. There was no evidence of investigation of potential contamination emanating from the site. Aspects like pipework were not investigated. From the reports on the Shell site it was apparent that remediation works were restricted to removal of obvious oil product contaminated materials. Buchanan (CE) Ltd's conclusion in the Stage 1 Desk Study was to undertake a geophysical survey together with trial pits, soil boreholes, rock boreholes, soil tests and chemical tests. The geophysical approach was to locate areas of potential interest, such as pipes and contamination plumes to guide the intrusive investigations.

ELECTROMAGNETIC GEOPHYSICAL SURVEY

Edinburgh University's Department of Geology and Geophysics was commissioned by the Council to undertake an electromagnetic survey using a Geonics EM31 Soil Conductivity Meter. The instrument creates a changing magnetic field which induces electrical currents to flow into conducting sub-surface matter. It is capable of measuring the in-phase and out-of-phase (i.e. quadrature) with the primary field in the uppermost 6 m of ground. Set to measure soil conductivities it yields large anomalies when metallic work is present. The orientation of the instrument is an influence on the values e.g. if perpendicular to a metal pipe, a strong negative value is recorded, flanked by positive values. Therefore in a NE-SW phase, pipes appear as negative anomalies, and in the NW-SE phase, appear as high values. By dividing the site into areas and for each measuring the in-phase and quadrature values on a 2 m x2 m and, a full picture was built up (Figure 3). Ground proving of one of the strong linear anomalies running NW-SE by digging a trial trench to a depth of 1 m encountered a 125 mm diameter metal pipe, precisely under the associated anomaly. Ground proving of another linear anomaly where a pipe appeared to end with low conductivity, suggesting a contamination plume, revealed a broken pipe with tarry oil product emerging (Figure 4).

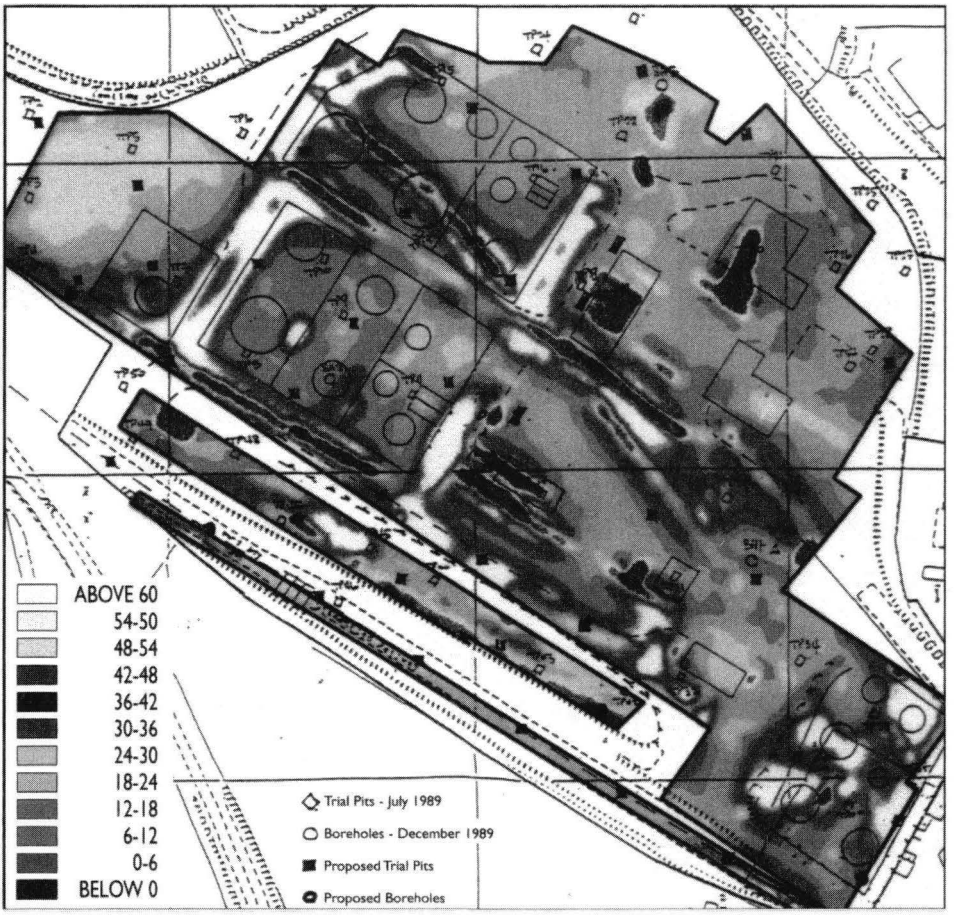

Figure 3
Electromagnetic Geophysical survey findings

From the composite anomaly map, a network of subsurface linear features appear present. By overlaying the base map it is possible to understand any correlations there may be with the original oil depot structures. The report concluded that further exploratory excavations will be required to confirm the presence of pipes and to help prepare reliable estimates of costs to remove them.

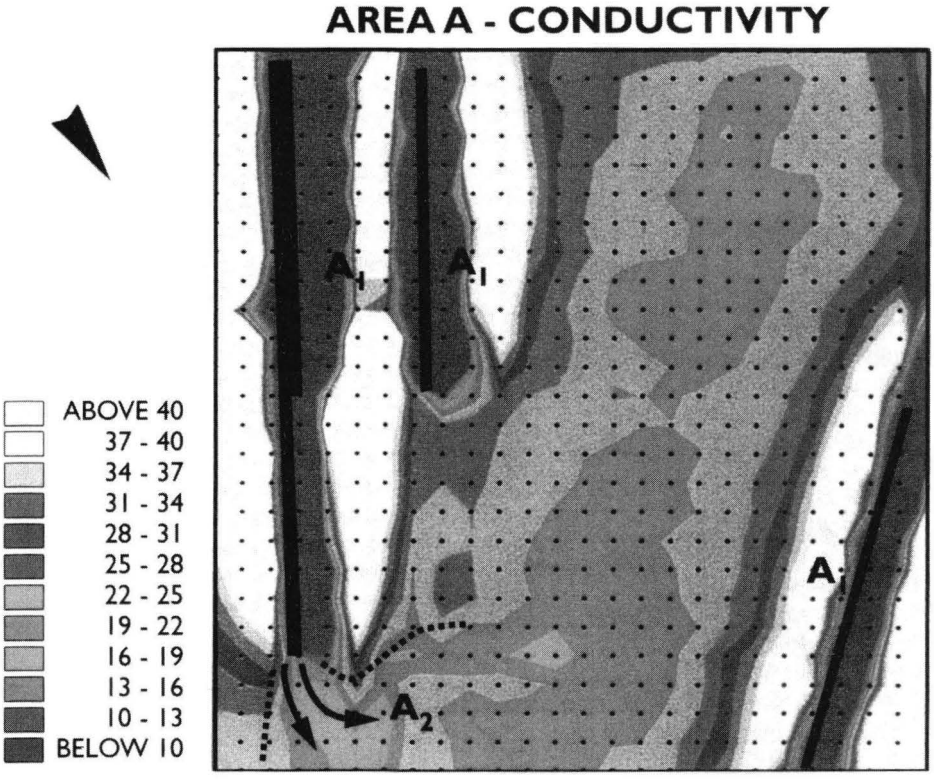

Figure 4
Contamination plume from pipe

STAGE 2 INVESTIGATION

From the trial pits, oil product contamination was evident by smell, petroleum products were seen in the ground water and occasionally signs of oils and tars. The area is generally covered by a cohesive material of poor permeability and the sandstones below were generally fractured. Whether the presence of faulted material could enable flow of ground water through bedrock was an issue that had to be addressed and a further survey to determine the hydrogeological conditions for contaminant transport beneath Granton was commissioned from the British Geological Survey in conjunction with the University of Edinburgh's Department of Geology and Geophysics.

HYDROGEOLOGICAL CONDITIONS STUDY

The study identified the presence of a sedimentary sequence of sandstones, shales and mudstones (the lower oil shale group), configured in a dome. Above is glacial till (boulder clay) and man-made ground, but at the northern end of the Granton Dome, the Granton Fault cuts across in a north easterly direction. Perched water is present in both the superficial deposits and ground water in the sandstones, which have bedding plane fissures. The hydrogeological conditions beneath are certain to be very complex. In general groundwater is moving northwards from the high ground at the south, being at a higher hydraulic head to the coast. A number of issues arose in terms of the extent of intrusion of pollutants into bedrock aquifers, their migration away from the site, their composition and the likelihood of them appearing at the surface in the future. The study highlighted an immediate need to determine the variable thickness of each rock/soil layer across the Texaco/Shell site, the precise locations of identified and unidentified faults and the extent of pollution migration laterally away from the site.

A PARALLEL APPROACH TO ASSESSING RISK

Three work streams thus ran in parallel. The ongoing Stage 2 Site Investigation, a resistivity geophysical survey and a laboratory determination of flow and contamination transport parameters for lithologies beneath the Texaco/Shell site.

STAGE 2 FINDINGS

Chemical testing confirmed the presence of significant petroleum product contamination on the Texaco site. 37% of the trail pits tested were above Dutch intervention levels, and 58% between target and intervention levels. Phenols, total PAHs, cyclohexane extract and volatile hydrocarbons were not significant either in the soil or water. The Shell site generally reflected the clean up that had already taken place. One rock borehole in a low lying area on the north boundary contained diesel contamination above the maximum concentration for Class 3 surface water. The conclusions were that the Texaco site and part of the Shell site is affected by significant petroleum product contamination. The products of most concern are the middle distillates, namely diesel and kerosene. The prevalence of hydrocarbons, the discontinuous nature of the made ground, the pending introduction of Section 57 of the Environmental Protection Act, all emphasised the need to act sustainably. Removal of all contamination above intervention levels is therefore the preferred remediation solution.

BIOREMEDIATION SOLUTION

A series of remediation options were assessed, excavation and removal, containment, soil venting and bio-remediation. Only the bio-remediation technique was considered sustainable for non-volatile hydrocarbons and has the advantage of retaining the material on site. This would involve excavation, on-site testing for selection, removal to an area, aeration by rotating techniques to encourage the rate of biological activity by increasing oxygen concentration, and then replacement to new profiles for development use. Excavation would be from ground level to depths in excess of 3 m but before this begins, the large network of underground metal pipes, which appear to contain either residues of petroleum products or water contaminated by the same, would have to be removed. This approach would ensure that there are no unacceptable

liabilities left with either the Council or the future developers and would also avoid developers seeking recourse to the Council because of the level of contamination.

RESISTIVITY GEOPHYSICAL SURVEY

The second workstream, the resistivity geophysical survey was to determine specific details about the subsurface, with the aid of available borehole data, and to assess the risk of contaminants emerging on the foreshore at Granton. It was designed to:

- evaluate the integrity of the superficial clay as a barrier
- locate any significant faults and connected permeable sequences
- delineate the saline/fresh water interface and predict the impact on groundwater.

The resistivity method involves the injection of a current into the ground and the measurement of the resulting potential differences at the surface. The method used was the Wenner Configuration where the current and potential electrodes are maintained at an equal separation. The Geopulse resistivity imaging equipment performs both the vertical electrical soundings and constant separation traversing, producing a two-dimensional slice through the subsurface. It is computer controlled. Contour plots allow data from all profiles surveyed to be viewed together, producing an overall picture. This allows interpretation of the data as a series of horizontal slices of resistivity variations through the sub-surface. Calculation gives the apparent resistivity as the average of the time resistivities sampled by the current. The positioning of the profiles was determined by the topography and the availability of open ground and correlated to the existing boreholes, in order to assist in assigning resistivity values.

RESISTIVITY GEOPHYSICAL FINDINGS

The clay coverage assessment showed some different characteristics associated with the clay, which could be a layer of sand and gravel with thin layers of clay either side. Generally the clay coverage was found to be adequate, but within four discrete zones further investigation is required because the results appear at variance with the Stage 2 findings. A major fault was detected which had not been previously identified and the suggestion of further small faults were noted (Figures 5 and 6). The survey attempted to investigate whether or not the fault extends to the foreshore north west of the site, but limited access and the short duration of low tide made this impossible. It was not proved that this fault is acting as a contaminant pathway. The saline interface is not a sharp boundary and therefore can not be pinpointed, but there is evidence to suggest the location of the transition zone is close to the north boundary, where fresh water may rise and discharge at the surface. Access and the triangular nature of the Texaco/Shell site proved to be a limitation on the survey. Time domain electromagnetic techniques (TDEM) could have been employed to cover the zones where no information was obtained but time prevented this.

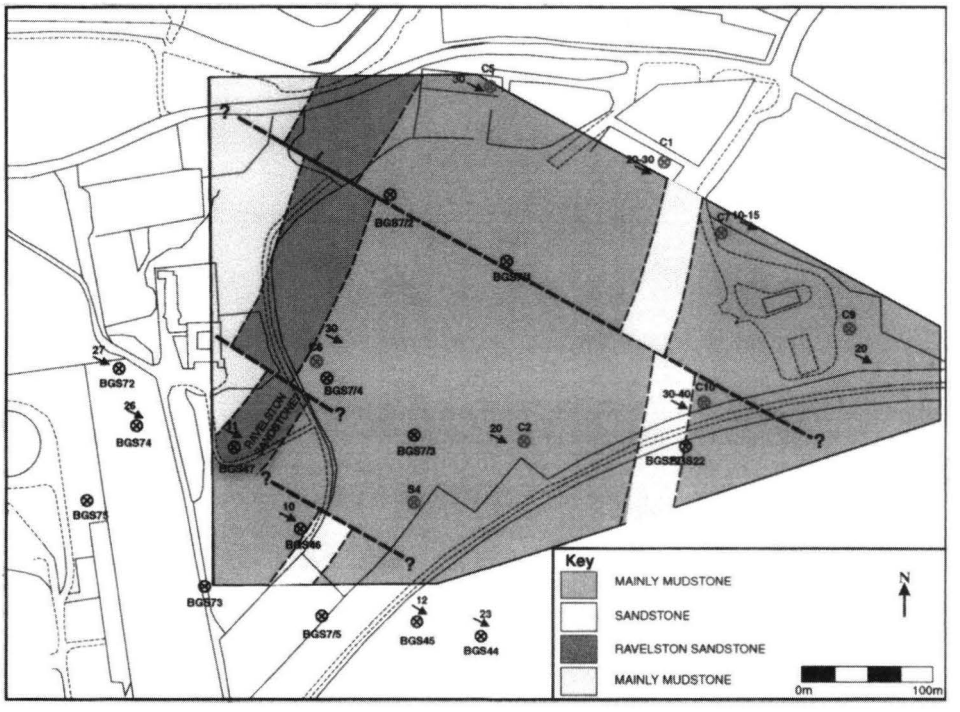

Figure 5
Faults found by resistivity geograpical survey

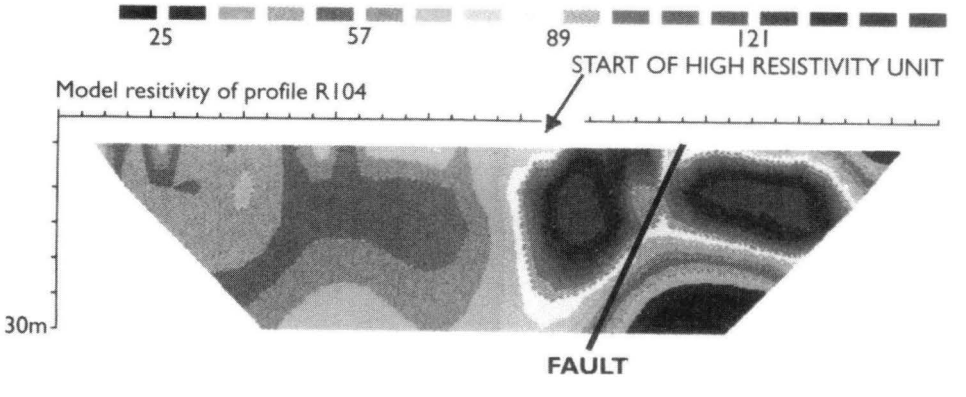

Figure 6
Vertical soundings along fault

FLOW AND CONTAMINANT TRANSPORT STUDY

The third workstream was to provide data on the flow and transport properties of sedimentary rocks beneath Texaco/Shell. It was specifically to establish:

- Data on porosity and permeability of core samples
- Data on dispersion and retardation coefficients of hydrocarbons
- Analytical data, including mineral composition and organic content of the rock, which have a bearing on adsorptive retardation of hydrocarbons.
- Assessment of underlying science and the migration velocities of the contaminants

The laboratory results show that the sandstones have very low porosities and permeabilities and are likely to be aquicludes. The lithologies showed that the sandstones are likely to strongly attenuate low concentrations of dissolved hydrocarbons, but to what extent the limited solubility of hydrocarbons will prevent adsorption and thus allow contaminants to leak through was not established. Within the sandstone aquifer, significant longitudinal dispersion was found, which could dilute contamination concentrations downstream to below pollution levels, but if the concentration is high, could cause a breakthrough of the pollution plume. Measurements did not take account of the effect of fractures and joints in the sandstones. Significant fracturing was noted but it was considered that more detailed laboratory fracture flow analysis would be needed to create robust data.

RISK ASSESSMENT

The overall recommendation from the University of Edinburgh's Department of Geology and Geophysics was that a hydrogeological model of the site should be set up to predict the migration and dispersal of hydrocarbon contamination. The question for the Council was whether the level of risk associated with the contaminants was acceptable or unacceptable and whether or not further investment in proving the robustness of the data is necessary. The critical factor was whether the regulator, Scottish Environment Protection Agency (SEPA) would set a standard for dissolved hydrocarbon contamination that would require more data to be gathered. Discussion with SEPA on the findings of the Stage 2 Site Investigation concluded that a maximum of 3.0 mg/l for free hydrocarbons in the groundwater would be the standard required. As all the sandstone boreholes were tested at levels below this, except for one ambiguity which is being monitored, the conclusion is that the level of risk is acceptable, particularly as the source of the hydrocarbon contamination will be subject to bioremediation. The effect of the clean up should therefore reduce and dilute the hydrocarbon presence in the ground water.

GRANTON GASWORKS

The Granton Gasworks is the largest individual site in the project. From 1890 gas was produced from coking coal. Today it is a storage facility for the supply of North Sea gas to the City and the landward towns. It is a major facility with three large capacity gas holders and falls into the major risk category of hazardous installations. The site is known to be heavily contaminated and constrained by the layout of the gas supply system. Without an investment in rationalising the gasworks, an investment in decontaminating the site for new use would be ineffective. An integrated

rationalisation and decontamination approach is the only way to unlock the potential of the site, but it must continue to provide the City's gas without interruption. The effect of working on the supply system in winter, the peak demand time, and the timescale of the Challenge Funding money are further constraints to be taken into account.

BRITISH GAS DEVELOPMENT STUDY

Following internal re-organisation in Spring 1997, British Gas Properties Plc indicated that they had no long term development aspirations and were willing to dispose of the non operational land to the Council, on terms to be agreed. From their development study, the costs of decontamination could vary within a band of plus or minus £1.0M, but the cost associated with relocating the gas pipes would clearly be a major factor in the overall redevelopment costs (Figure 7).

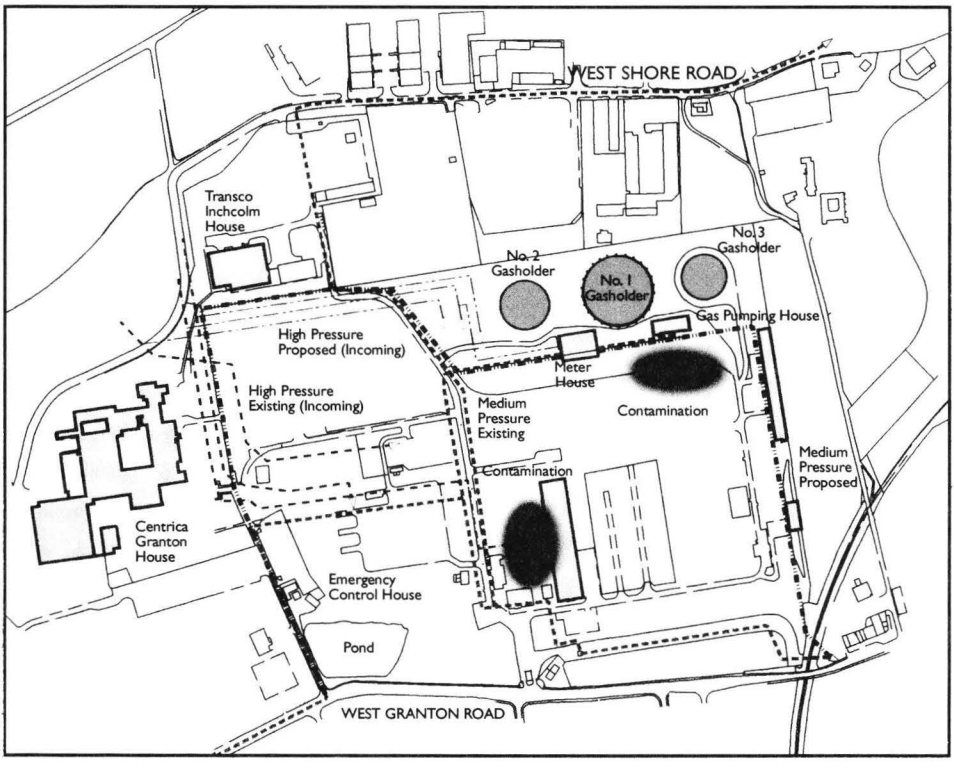

Figure 7
Granton Gasworks

Depending on what option was selected, the costs could be as high as £35M if the gas holders were removed. The Council jointly with LEEL and British Gas Properties agreed that advancing design and tender preparation of the pipework was essential because it has a bearing on the programmes for decontamination and for construction of the new southern access road that will provide the link to the strategic road network.

British Gas's development study identified significant contamination from spent oxide. The areas lie within and immediately adjacent to those parts of the site that were historically the gas purification houses. It is 3 m deep and poses a potential hazard to ground and surface water. Options for treatment range from encapsulation within the site which impacts upon future land use, cleaning through a soil washing process, or disposal to landfill. The study also highlighted hot spots of residual contamination associated with old tar, liquor and gas pipework up to 6m below ground. Adjacent to one of the retort buildings was a significant amount of oil product contamination associated with an old storage tank. Their estimate for decontaminating the site was within a £5.0M - £6.0M band of costs, depending on the option selected. What was evident from this study was that the gas pipeline work would cut through or run alongside these contamination areas and hot spots.

GASWORKS RATIONALISATION

The gasworks rationalisation involves a family of different sized pipes at different pressures, metering, jet boosting, electrical apparatus and commissioning and decommissioning. Regular joint meetings of the Council, British Gas Properties, Transco, their pipeline consultants and the Council's appointed independent pipeline consultants, were needed to guide Transco on where to align the new pipes. The work by consultants on the economic impact study and by the Council on the new access road has given confidence in projecting the future development pattern and the alignment of the new 1200 mm medium pressure gas pipeline and the other smaller pipelines to reflect this layout. Tenders are now ready for issue on a design and build basis, the actual issue date depending on the Council and British Gas Properties agreeing heads of terms for the land acquisition. If agreement is delayed, the knock on effect will be to push the commissioning of the new supply system into next year's winter peak demand period.

INTEGRATED APPROACH

The gasworks rationalisation highlights the need to undertake specific decontamination work prior to pipework construction. With the new access road commencing construction and working northwards, all decontamination, pipework rationalisation and road construction activity has to be completed by the end of March 2000 before Challenge Funding runs out. As a condition in the heads of terms the Council will have to commission its own independent study of the decontamination works required and will then have to reach joint agreement on the precise schedule of works with British Gas. The timescale for independent study and agreement is therefore critical. The heads of agreement place responsibility on the Council as developer and statutory control authority for the decontamination costs, the standards and the attendant risks. British Gas Properties accepts a element of responsibility for

statutory clean up and will contribute a significant sum towards the decontamination works.

CONCLUSION

This is a snapshot picture of progress on the North Edinburgh Project from March 1997 to February 1998. It is a project that has to work at two levels, locally and at a city level and physically on two levels as well. It is about integration of the derelict land into the community and integration of the Waterfront into the City. Many parallel stands are being promoted simultaneously to help deliver the project and the benefits of this approach are:

- Partnership working with LEEL, Scottish Homes, British Gas Properties plc, and Boland Scottish Properties is developing and with the establishment of the Council's Special Projects Team and a partnership agreement with LEEL, the targets set for this Challenge Funded project will be delivered to programme.
- Community participation in the Council's development aspirations is helping to build up a dialogue and begin the process of engaging the community as a "real partner".
- Using the principal community organisation, the Pilton Partnership brings access to a range of communication and publicity mechanisms which will up the confidence level of the community in the Council's ability to deliver.
- The early implementation of the economic impact study, before reclamation design has begun, will ensure that land use design decisions fit the emerging long term vision for the Waterfront and have the support of the wider City property market.
- Dialogue with the regulators, SEPA in particular, during the site investigation process, creates a channel for joint ownership of the contamination and ground water problems and engenders willingness by both parties to ensure solutions are balanced and sustainable.
- Capitalising on the Council's Town and Gown Initiative with the University of Edinburgh, has given access to a range of methodologies that have complimented the site investigations of the Texaco/Shell Oil depots and allowed a broader assessment of risk to be undertaken than might have been the case under a traditional civil engineering approach.
- The geophysical methodologies utilised have encouraged the Council to collaborate further with the University of Edinburgh on the application of GIS to create a total geophysical approach to ensuring substrata pathways do not affect development.

A more detailed picture will be presented at the conference, by which time the actual sequence of events will be known and hopefully work will have begun on the decontamination of this exciting project.

ACKNOWLEDGEMENTS
This paper represents the views of the author which are not necessarily those of The City of Edinburgh Council. The author wishes to thank I Kerr, R Barclay, D Slee and E Dunn of the project team, Chris Bushe, Graphic Designer, and N Buchanan of Buchanan (CE) Ltd for their assistance and helpful comments.

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COMPLETE BIODEGRADATION OF RDX AND HMX IN ANOXIC SOIL SLURRY BIOREACTORS: LABORATORY AND PILOT-SCALE EXPERIMENTS

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Key words: bioremediation, biodegradation, slurry bioreactor, explosive, microcosms, soil, treatment, anaerobic

SUMMARY
Nitramine explosive degrading and mineralizing activity of indigenous microbial population in anaerobic sludge and soil were studied in microcosm tests under various conditions. Indigenous microbial populations in soil from an explosive contaminated site were unable to mineralize RDX or HMX to any great extent. In contrast, anaerobic sludge was an excellent source of explosive degrading microorganisms. Supplements of anaerobic sludge in soil slurry microcosms significantly enhanced the mineralization extent of RDX (800 ppm) and HMX (267 ppm) up to 60%. The anoxic bioslurry process degraded nitramine explosive rapidly and is considered as a feasible technology for the remediation of nitramine explosive highly contaminated soil.

KURZFASSUNG
Der Abbau von explosivem Nitramin und seine Minersalisierung durch endogene Mikrobenpopulationen in anaeroben Schlämmen und Böden wurde in Mikrokosmostests unter verschiedenen Bedingungen untersucht. Die endogene Mikrobenpopulation von explosionskontaminierten Böden konnte weder RDX noch HMX zu einem erkenntlichen Mass mineralisieren. Dagegen waren anaerobe Schlämme eine hervorragende Quelle für Explosionsstoff abbauende Mikroorganismen. Der Zusatz von anaeroben Schlaemmen zu Bädensuspensions-Mikroorgansimen verbesserte die Mineralisierung der Explosionsstoffe zu 60%. Der anoxische Biosuspensionsprozess baut Explosiva schnell ab und ist eine brauchbare Technologie für die Regerneration von hochgradig mit Nitraminexplosivstoffen kontaminierten Böden.

RÉSUMÉ
L'activité de dégradation et de minéralisation d'explosifs nitraminés par des populations bactériennes indigènes de sols contaminés et de boues municipales anaérobies a été étudiée sous différentes conditions en microcosmes. Les populations indigènes de sols contaminés aux explosifs étaient incapables de minéraliser significativement le RDX et le HMX. Par contre, l'ajout de boue municipale anaérobie aux sols en microcosmes a augmenté de façon importante le niveau de minéralisation pour le porter à 60 %. Il semble donc que la boue municipale anaérobie contenait des souches dégradant les explosifs. Les résultats obtenus avec le réacteur rotatif anoxique en phase bouense démontrent que cette technologie convient bien au traitement de sols hautement contaminés aux explosifs nitraminés.

Contaminated Soil '98, Thomas Telford, London, 1998, 513–522

INTRODUCTION

Hexahydro-1,3,5-trinitrio-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) are the most important and powerful military high explosives in the world today. Both RDX and HMX are commonly present together in contaminated sites where manufacturing and military exercises were conducted in the past. RDX and HMX are toxic[14,15] and persistent in the natural environment. The toxicity and persistence of these nitramine explosives in contaminated sites threaten human and environmental health. Consequently, the soil contaminated with these explosives must be remediated.

Biodegradation studies of RDX and/or HMX can be dated back to 1970s. Early work showed that RDX was persistent under aerobic conditions[7]. Until recently, some microorganisms were found to be capable of utilizing RDX and HMX as nitrogen sources[3,6,8]. The fate of RDX and/or HMX under anaerobic conditions was investigated by a number of researchers[12,13,17] in the 1970s and 1980s. Pure cultures with the capability of degrading RDX and/or HMX have been recently isolated[4,10,18]. In these studies, the experiments only demonstrated either biotransformation or poor mineralization of the explosive. Anaerobic degradation of RDX and/or HMX has also been demonstrated in soil slurry processes[5,9] and soil columns[11]. However, the concentrations of RDX and HMX in these contaminated soils were relatively low in these studies, and the fate of the contaminant (such as mineralization, binding of metabolites to soil matrix) was not well characterized.

The goal of this research was to study the explosive degrading activity of microorganisms from different sources, and to search for optimal conditions for the degradation of RDX and HMX in contaminated soil toward pilot-scale operations of a bioslurry reactor. Another research objective was to investigate the fate of the explosive and its metabolites during the degradation processes.

MATERIALS AND METHODS

Sources of microorganisms: Microorganisms were indigenous microbes in a sandy soil collected from munitions burning pits at Angus, Ontario, Canada, but neither HMX nor RDX was detected in this soil. Municipal anaerobic sludge from the wastewater treatment plant of Vaudreuil, Quebec, Canada, was used as potential exogenous sources of explosive degrading microorganisms.

Chemicals: Commercial grade HMX and RDX (with a purity > 99%) were provided by Defense Research Establishment Valcartier, Quebec, Canada. [^{14}C]-HMX and [^{14}C]-RDX with respective specific activities of 93.3 and 28.7 μCi/mmole were synthesized and purified (99%) as described by Ampleman *et al.*[1].

Mineralization of RDX and HMX: Anaerobic sludge and soil slurry microcosms were conducted to study the explosive mineralizing activity of indigenous microorganisms in anaerobic sludge and soil. The anaerobic sludge microcosms were prepared as follows: a series of 100 ml serum bottles were filled with a various amounts of unlabeled RDX or HMX in acetone solution, and spiked with 20 μl of [^{14}C]-RDX or [^{14}C]-HMX acetone solution to give a final radioactivity of about 100,000 dpm. After evaporation of the acetone, 39 ml of the municipal anaerobic sludge and 1 ml of molasses feed were added

to the serum bottles. A CO_2 trap composed of a test tube containing 1 ml of 0.5M KOH was also placed inside the serum bottle. The serum bottles were purged with nitrogen, and sealed by butyl rubber stoppers and aluminum crimps prior to incubation at 28°C on a rotary shaker (150 rpm). The molasses feed contained (g/L): 33.1 g of molasses, 7.4 g $NaHCO_3$ and 8.8 g $KHCO_3$. Parallel microcosms that were not supplemented with [^{14}C]-RDX or [^{14}C]-HMX were also set up for chemical analysis of RDX or HMX and their metabolites along the course of the experiment.

The soil slurry microcosms were prepared in a similar way to that of the anaerobic sludge microcosms. Briefly, the microcosms were charged with 16.0 or 28.0 grams of the sandy soil (dry weight), 1 ml of the molasses feed, and 8 ml of the municipal anaerobic sludge. The total weight of the soil slurry in the serum bottle was completed with distilled water up to 40 g. In this soil slurry, the soil made up 40% or 70% (w/w) of the 40 grams, while the sludge made up 3.3 to 4.6 g of volatile suspended solids (VSS) per kg slurry. All microcosm tests were performed in triplicate and sampled regularly. [^{14}C]-radioactivity in the KOH absorbent was counted in a TRi-Carb® liquid scintillation analyzer (Model 2100 TR, Packard Instrument Company, Meriden, CT).

Analysis and identification of RDX, HMX and their metabolites: Metabolites in the microcosms that did not receive radiolabel were extracted using acetonitrile. Analysis was carried out by an HPLC (Spectra-Physics Model SP8100, Thermo Separation Products, California, Inc.) equipped with a Supelcosil CN column and a 254 nm UV detector. The identification of RDX metabolites was performed by comparing with standard compounds. HMX metabolites were identified by a Platform LC/MS (Micromass UK Limited, Wythenshawe, UK) using a negative electrospray ion source.

Distribution of [^{14}C]-RDX, [^{14}C]-HMX and their metabolites in soil slurry: Soil slurry microcosms were set up according to the procedures described in the mineralization study except that these microcosms contained 16.0 g of soil, and RDX and HMX concentrations were 800 and 267 mg/kg, respectively. The portion of RDX or HMX mineralized was quantified by counting the radioactivity of liberated $^{14}CO_2$. The acetonitrile extractable portion of the radiolabel and the part of the radiolabel binding to the soil matrix in the soil slurry was assayed by the method described by Shen *et al.*[16].

Remediation of RDX and HMX contaminated soils in bioslurry reactors: Biodegradation of a clay soil highly contaminated with RDX (1180 mg/kg dry soil) and HMX (700 mg/kg dry soil) was studied in a drum-style slurry bioreactor with a volume of 8 liters. The soil was mixed with feed and sludge to create a soil slurry with 44% solids content. The reactors were operated at 35°C and with continuous rotation.

RESULTS

RDX and HMX degrading activity of municipal anaerobic sludge. The data in Figure 1 shows the disappearance of RDX with time. At RDX concentrations of 50, 420 and 870 ppm, the time required for complete disappearance of the explosive was 2, 14 and 28 days of incubation, respectively. The data from parallel microcosms spiked with [^{14}C]-RDX reveals that 0.65, 121 and 385 ppm of RDX were respectively recovered as CO_2 on the above mentioned days in these three microcosms. The RDX mineralization

extent kept progressing even after the RDX concentration in the sludge reached zero. Further incubation till 50 days increased the RDX mineralization to 30.3, 272 ppm and 545 ppm of RDX, respectively (Fig. 1). The data in Figure 1 also reveal that the mineralization rate of RDX into CO_2 was slower than its degradation rate, and the maximum RDX mineralization rates were maintained in the microcosms up until a few days after the RDX concentration in the sludge reached zero. The total amount of mineralized RDX increased with the increasing RDX initial concentration in the anaerobic sludge. The lower the RDX concentration in the sludge, the more rapidly the RDX mineralization rate reached a plateau.

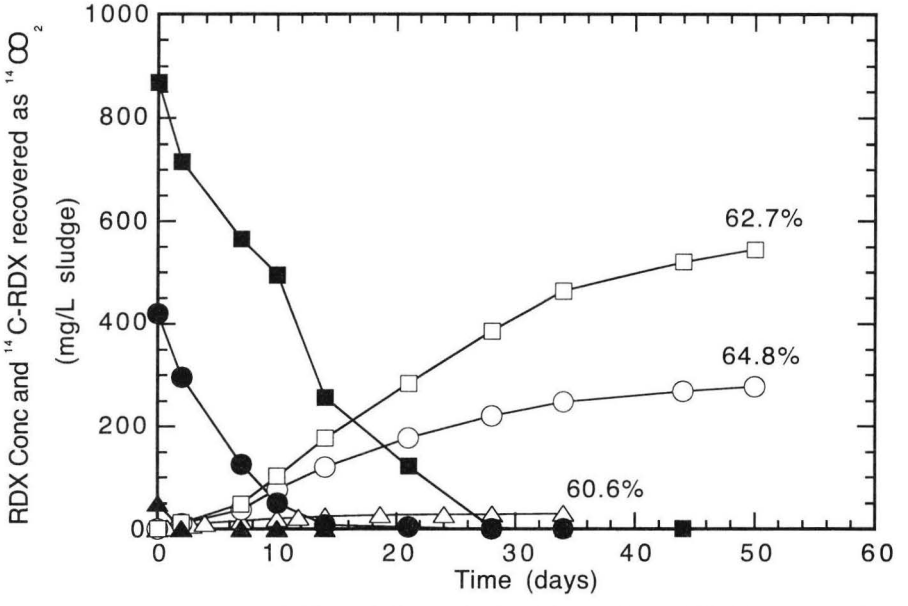

Figure 1. A time course of RDX degradation and mineralization in municipal anaerobic sludge (8.95 gVSS/L) at 26°C. Residual RDX in the microcosms with initial RDX conc. of 870 ppm (■), 420 ppm (●), and 50 ppm (▲); RDX mineralized into CO_2 in the microcosms with initial RDX conc. of 870 ppm (□), 420 ppm (○) and 50 ppm (Δ).

Unlike the RDX mineralization, the data in Figure 2 shows that there was a relatively long lag period (14 days) in the HMX mineralization in the anaerobic sludge. The maximum HMX mineralization rates in the samples with respective HMX concentrations of 250 and 500 ppm were 0.36 and 0.40 mg HMX/(g VSS.d), and were maintained until days 30 and 60, respectively. Whereas, the maximum mineralization rate in the microcosm with 25 ppm HMX was lower [0.07 mg HMX/(g VSS.d)].

RDX and HMX metabolites in anaerobic sludge. HPLC analysis of supernatant from the sludge supplemented RDX reveals that at least 6 metabolites were formed. One metabolite has been identified as nitroso-RDX by comparison with standards. Several metabolites were also found in the sample from the anaerobic sludge amended with HMX. Three metabolites showed strong molecular ions at *m/z* 279, 263 and 247,

respectively. These molecular ions corresponded to the molecular weights (M-1) of mono-, di- and trinitroso-HMX. However, other metabolites have yet to be identified.

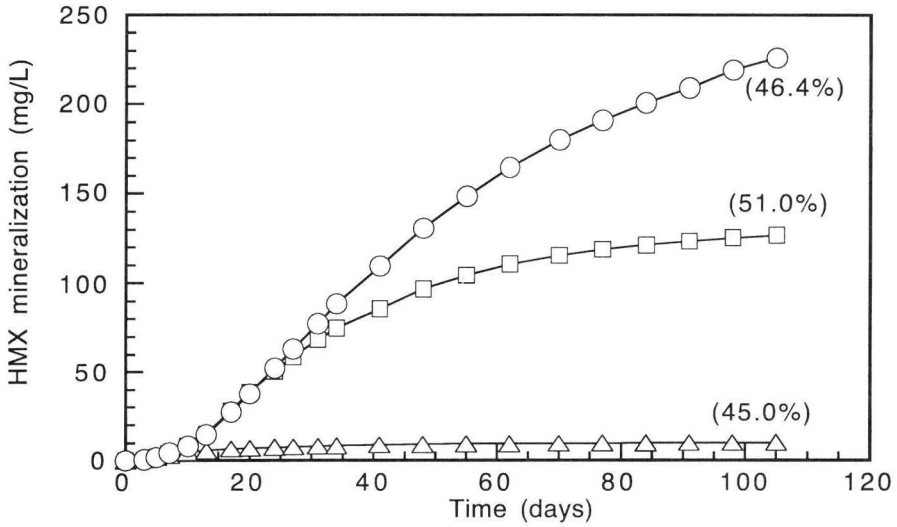

Figure 2. A time course of HMX mineralization in municipal anaerobic sludge (4.23 gVSS/L) with various initial HMX concentrations (○, 500 ppm; □, 250 ppm and Δ, 25 ppm) at 28°C.

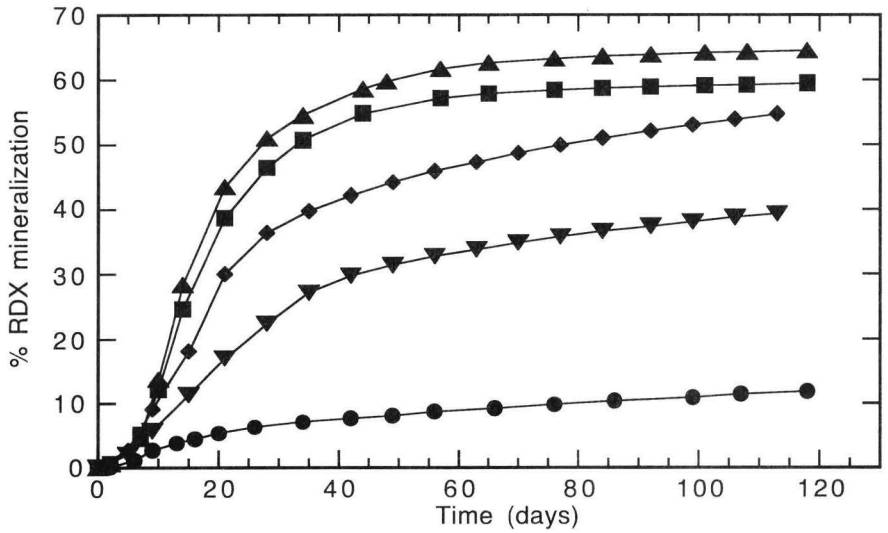

Figure 3 Mineralization of RDX in soil slurry microcosms under various conditions (●, 40% soil and 800 ppm RDX; ■, 40% soil, 0.46% sludge (VSS) and 800 ppm RDX; ▲, 40% soil, 0.46% sludge (VSS), 800 ppm RDX and 267 ppm HMX; ◆, 70% soil, 0.46% sludge (VSS), 800 ppm RDX and 267 ppm HMX; ▼, 70% soil, 0.46% sludge (VSS), 1400 ppm RDX and 467 ppm HMX)

RDX and HMX mineralization in the soil slurry. The mineralization of RDX in the soil slurry microcosms under various conditions is illustrated in Figure 3. About 12% RDX

(with an initial concentration of 800 mg RDX/kg slurry) was mineralized by an indigenous microbial soil population after 4 month of incubation. A supplement of exogenous anaerobic sludge containing explosive degrading microorganisms significantly enhanced the RDX mineralization rate and extent, reaching 58% after 4 months of incubation. Increasing the solid content of soil slurry in the microcosms resulted in negative impacts on the mineralization rate and extent of RDX. The negative effect of high solids content in the slurry may be attributed to the decrease of RDX mass transfer rate from the solid phase to the aqueous phase, limiting the availability of explosive to the microorganisms. Increasing explosive concentrations in the soil slurry did slow down the % mineralization, but did not decrease the mineralization rate. If the RDX mineralization data in Figure 3 were expressed in mg RDX/(kg slurry.d), the results would reveal that the maximum RDX mineralization rate was independent of the explosive concentration in the microcosms with the same solids content.

The mineralization profile of HMX was similar to that of RDX except that longer lag periods were observed in the later case especially when RDX was present in the soil slurry (Figure 4). The HMX mineralizing activity of indigenous soil microorganisms in an explosive contaminated soil was poor, and only 4% of HMX (at an initial concentration of 267 mg HMX/kg slurry) was mineralized after 4 months of incubation. Increasing solids content from 40% to 70% in the soil slurry had a negative impact on the percentage of HMX mineralization, declining from 55.4% to 40.2%. This decrease is slightly higher than that observed in the case of RDX (from 64.5% to 54.7%). However, the mineralization extent of HMX declined to 20.3% when the concentrations of both RDX and HMX were increased to 1400 and 467 ppm respectively in the soil slurry, which is more significant than the decrease (to 39.3%) in the case of RDX mineralization.

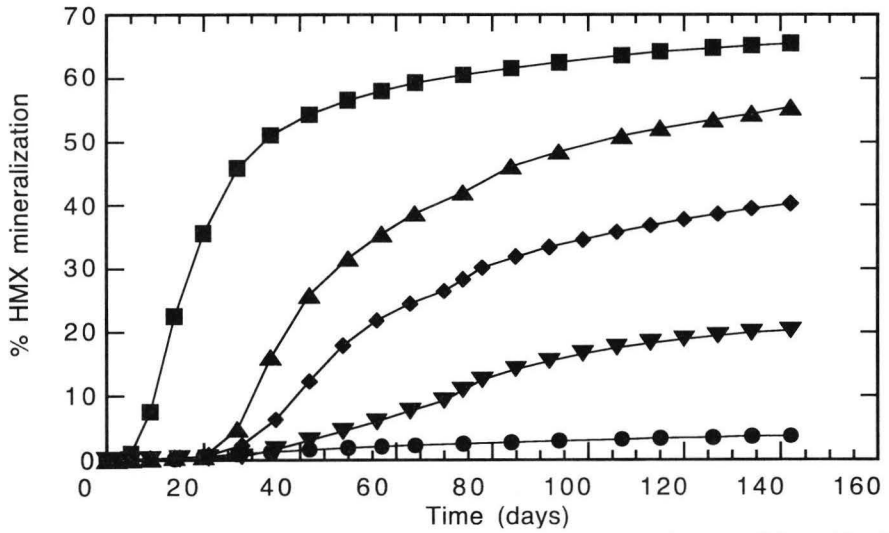

Figure 4 Mineralization of HMX in soil slurry microcosms under various conditions (●, 40% soil and 267 ppm HMX; ■, 40% soil, 0.34% sludge (VSS) and 267 ppm HMX; ▲, 40% soil, 0.34% sludge (VSS), 267 ppm HMX and 800 ppm RDX; ◆, 70% soil, 0.46% sludge (VSS), 267 ppm HMX and 800 ppm RDX; ▼, 70% soil, 0.46% sludge (VSS), 467 ppm HMX and 1400 ppm RDX)

Partitioning of RDX and HMX in the soil slurry. The microcosms prepared for the RDX and HMX partitioning study contained both unlabeled RDX (800 ppm) and HMX (267 ppm) and was supplemented with either [^{14}C]-RDX or [^{14}C]-HMX (about 100, 000 dpm). The RDX and HMX partitioning data in Table 1 reveals that, as expected, the %RDX and HMX mineralization (as measured by $^{14}CO_2$ production) increased over the incubation time. Meanwhile, more radiolabel from HMX was assimilated into biomass. About 15% of the radiolabel from HMX became acetonitrile non-extractable after 7 weeks of incubation. The non-extractable portion of radiolabel in the tested RDX microcosms fluctuated over the incubation period, however, the mass balance of radiolabel indicates that the non-extractable portion (incorporated into biomass and/or bound to soil matrix) was less than 6%. A significant portion of radiolabel (28% to 34%) remained extractable in the microcosms after 7 weeks of operation. Chemical analysis results from parallel microcosms without receiving radiolabel indicate that this extractable radiolabel was neither RDX nor HMX. A reasonable mass balance was obtained, with recovery of 88% to 100.1% of radiolabel in various samples over the experimental time period. Good recoveries of radiolabel suggest that the amount of radiolabel converted into $^{14}CH_4$, which was not measured in the experiment, was not a major portion.

Table 1 Partitioning of RDX and HMX in soil slurry

Cumulative time (days)	% RDX & metabolites extractable	% CO_2	% ^{14}C non-extractable	% ^{14}C recovery
0	96.0	0	1.5	97.5
2	93.8	0.9	3.2	97.9
7	79.6	4.9	6.1	90.7
14	60.8	22.8	4.1	87.7
24	41.8	42.8	4.0	88.8
34	29.2	57.3	2.0	88.6
48	28.1	59.1	5.9	93.0
Cumulative time (days)	% HMX & metabolites extractable	% CO_2	% ^{14}C non-extractable	% ^{14}C recovery
0	98.8	0	1.3	100.1
6	97.9	0.2	N.D.	98.1
13	96.8	0.5	N.D.	97.3
27	81.4	8.2	8.5	98.6
37	51.9	29.1	16.3	97.3
48	34.3	46.1	14.9	95.3

N.D.: not done

RDX and HMX degradation in bioreactors. Figure 5 shows that all RDX (2000 mg/kg slurry) was degraded after only 5 days of operation, while the removal of HMX (1600 mg/kg slurry) shows a lag period. These results are consistent with the results obtained during the microcosm mineralization study. No metabolites were detected after one month of operation.

DISCUSSION

The production of $^{14}CO_2$ from [^{14}C]-RDX and [^{14}C]-HMX degradation in the anaerobic microcosms with soil and/or anaerobic sludge indicated that indigenous microorganisms in soil and anaerobic sludge were able to mineralize RDX and HMX to CO_2, although the %mineralization may depend on the microbial activity in the samples. The nitroso RDX and HMX metabolites observed from the RDX and HMX degradation were also detected earlier[10,12,13,18]. However, no mineralization of RDX or HMX was detected by McCormick *et al.*[12,13], and less than 10% of RDX with an initial concentration of 33 ppm was mineralized by pure cultures after 45 days of incubation in Kitts et al's experiment [10]. Crawford *et al.* [4] also isolated microorganisms which were able to degrade RDX, but no metabolite identification was carried out.

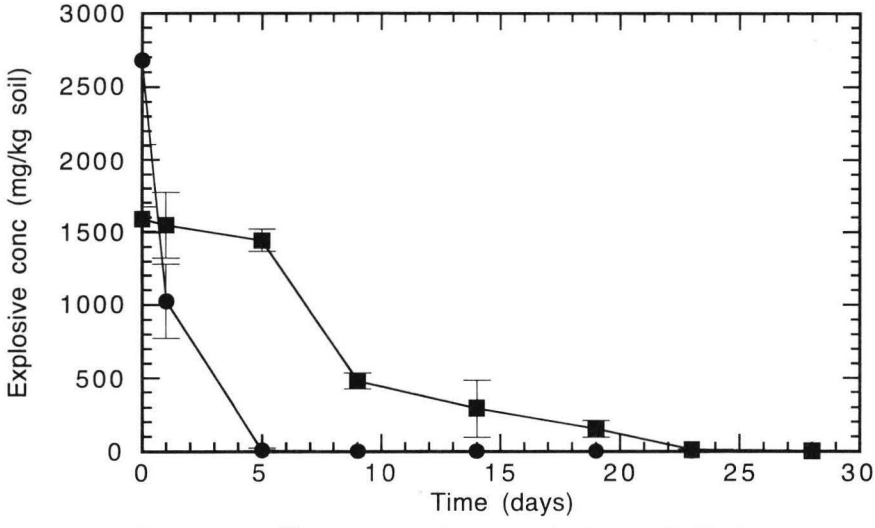

Figure 5 RDX (●) and HMX (■) degradation in an anoxic drum-style bioslurry reactor with 44% solids content, rotated continuously and maintained at 35°C

Figure 1 shows that the RDX disappearance was much faster than the mineralization ($^{14}CO_2$) rate. The concentration profiles of RDX and CO_2 in Figure 1 revealed that the RDX mineralization process likes a series of first-order reactions where the conversion rate of RDX to intermediate(s) was faster than the conversion rate of intermediate(s) to a final product $(CO_2)^2$. This result was consistent with those reported by Young *et al.*[18] who reported that a sequential reduction of the three nitro groups in RDX follows first order kinetics and the reduction rate of the second and third nitro groups is lower. The RDX concentrations in the two microcosms (420 and 870 ppm) were much higher than its water solubility (40 ppm) during the first 10 days. The bioavailability of RDX in these two microcosms might not be very different during this period, implying that the RDX degradation rate would be similar in these two microcosms. This inference is supported by the data in Figure 1 where almost the same amount of RDX was degraded in the two microcosms during the first 10 days of incubation.

The similar mineralization percentage of HMX was observed in the two samples with respective concentrations of 250 and 500 ppm HMX before day 22 of incubation

(Figure 2). This may be attributed to relatively higher initial concentrations of HMX used in the microcosms. The HMX concentration of 250 and 500 ppm was 60 and 120 times, respectively, higher than its water solubility (4 mg/L). The high initial dosages of HMX would render its concentration over saturated for a certain time despite the occurring slow biodegradation, and showed no significant difference in the its bioavailability to microbes during the first month of incubation. Consequently, their mineralization rates were very similar.

While the RDX, HMX degradation and mineralization studies provided insight into the kinetics of explosive degradation in anaerobic sludge, the mineralization and partitioning studies of RDX and HMX in soil slurry microcosms illustrated the potential of the bioslurry process as a technology in the remediation of explosive contaminated soil. The poor mineralization of RDX and HMX in the microcosms with soil alone indicated that indigenous microorganisms may be insufficient to remediate RDX and HMX without the supplement of exogenous sources of explosive degrading bacteria. The experimental results also showed that RDX was easier to mineralize than HMX. A similar result was reported in a pure culture study[10]. This may be explained by the sequential utilization of nitrogen sources from RDX and HMX by microorganisms in the anaerobic sludge. HMX is less soluble and usually more resistant to microbial attack, which makes HMX more difficult to be used as nitrogen sources by microorganisms than RDX.

CONCLUSIONS

The mineralization of RDX and HMX into CO_2 in anaerobic sludge and a soil slurry under anaerobic conditions is a multi-step degradation process, which first involves a sequential reduction of nitro groups into nitroso groups. Municipal anaerobic sludge is an excellent source of RDX and HMX degrading microorganisms, and the anaerobic bioslurry process is able to completely degrade nitramine explosives in contaminated soils with extensive mineralization. Bioremediation of highly contaminated RDX and/or HMX soil under anaerobic conditions is feasible.

ACKNOWLEDGMENT

Authors thank Louise Paquet for excellent analytical services.

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ANAEROBIC / AEROBIC BIOREMEDIATION OF PCB-CONTAMINATED SOIL AND SEDIMENT

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Key words: bioremediation, PCBs, dechlorination, soil, sediment

INTRODUCTION

Polychlorinated biphenyls (PCBs) are a family of potentially 209 related chemical compounds synthesized by the direct chlorination of biphenyl. These compounds were manufactured and sold as complex mixtures (under trade names Aroclor, Phenoclor, Clophen, and Kanechlor) with formulations, produced for different applications, that differed in their average chlorine content. The individual PCB isomers, or PCB congeners, in these mixtures are referred to according to the position of the chlorine substituent (e.g., Figure 1). Obviously up to ten chlorine substituents could theoretically exist, although averages run between 5 and 7 generally. All 209 possible configurations are not available even in mixtures.

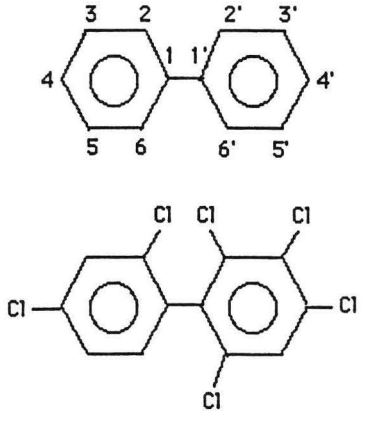
The desirable physical and chemical properties of PCBs (dieletric, flame resistence, thermal and chemical stability) led to their extensive industrial use as heat transfer fluids, hydraulic fluids, solvent extenders, plasticizers, flame retardants and dielectric fluids (Hutzinger, Safe, and Zitko, 1974). Extensive application of these chemically and thermally stable compounds has resulted in their widespread contamination of soils and sediments (Buckley, 1982). Several hundred million kilograms of PCBs have been estimated to have been released into the environment (Huzinger and Veerkamp, 1981) (Figure 2). Although, in general, PCBs are considerably hydrophobic, their octanol/water partition coefficients, Kow, range over 5 orders of magnitude from for example log Kow of 5.22 for a tricholorobiphenyl to 10.44 for a nonachlorobiphenyl. Hence, they tend to concentrate in sediments and soils. Their solubilities range from about 0.1 ug/L for decachlorobiphenyl to about 7500 ug/L for chlorobiphenyl. Yet, as the world's oceans represent the largest sink, although relatively dilute, they contain about 80 % of the PCBs found in the mobile environmental reservoir (Figure 3).

ANALYTICAL DIFFICULTIES

Critical to predicting the existance and fate of PCBs in the environment is an understanding of the range of chemical and physico-chemical characteristics. PCBs are not monolithic and different mixtures result in different behavoirs as a group and also as individual molecules (or congeners). For example, the vapor pressure of individual congeners is a function of the number of chlorine substituents but also the location of these chlorine substituents. PCBs with fewer chlorines and more ortho-chlorines tend to have higher vapor pressures. Higher vapor pressures are often correlated with chormatographic retention times (Figure 4). Due to this variablility in vapor pressure, several trends can be considered. The first is the effect this has on the volatilization of different congeners with time from soils causing a final chromatographic imprint inconsistent with commercial mixtures. The second is the chromatographic analyses themselves. The separation of all PCB congeners in a

Contaminated Soil '98, Thomas Telford, London, 1998, 523–530

Figure 1
General IUPAC structure and nomenclature of polychlorinated biphenyls, PCBs.



example : hexachlorobiphenyl # 139

Nomenclature :
IUPAC or Ballschmiter and Zell ( ) : 2,2',3,4,4',6- hexachlorobiphenyl
other nomenclatures : 2346-24 or 2,3,4,6,2',4'-

Figure 2 **Estimated U.S. Production, Utilization and Distribution of PCBs**

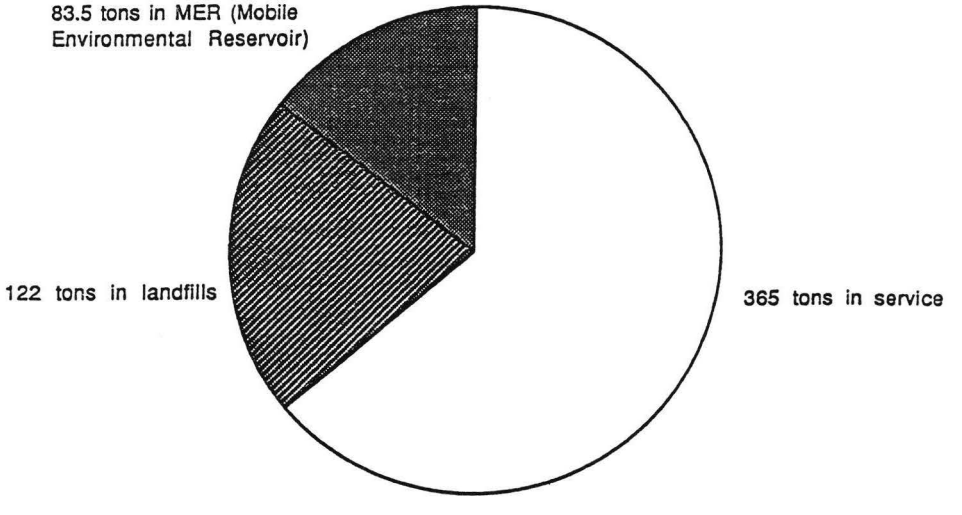
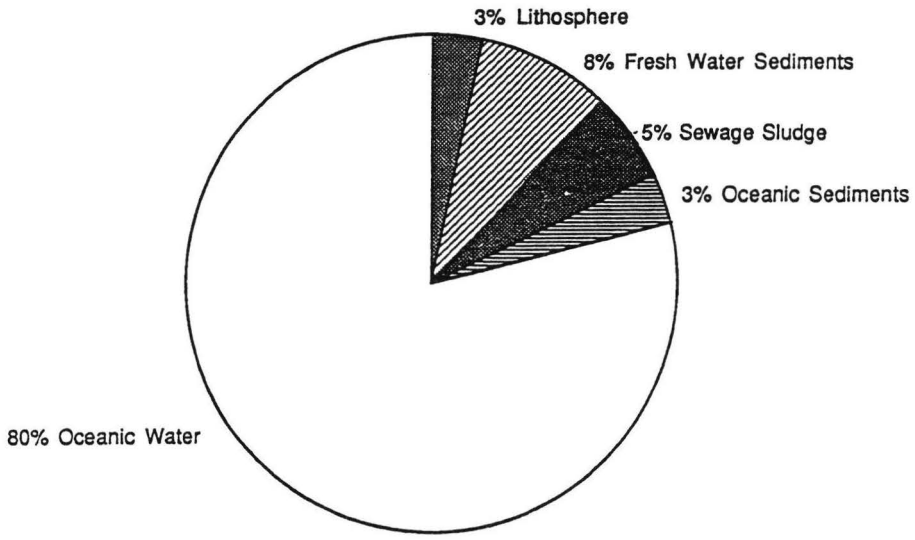


Figure 3 **Distribution of PCBs in the Mobile Environmental Reservoir***



* The atmosphere, fresh water, and biota in both fresh and oceanic waters contain less than 1% of the total PCBs present in the MER

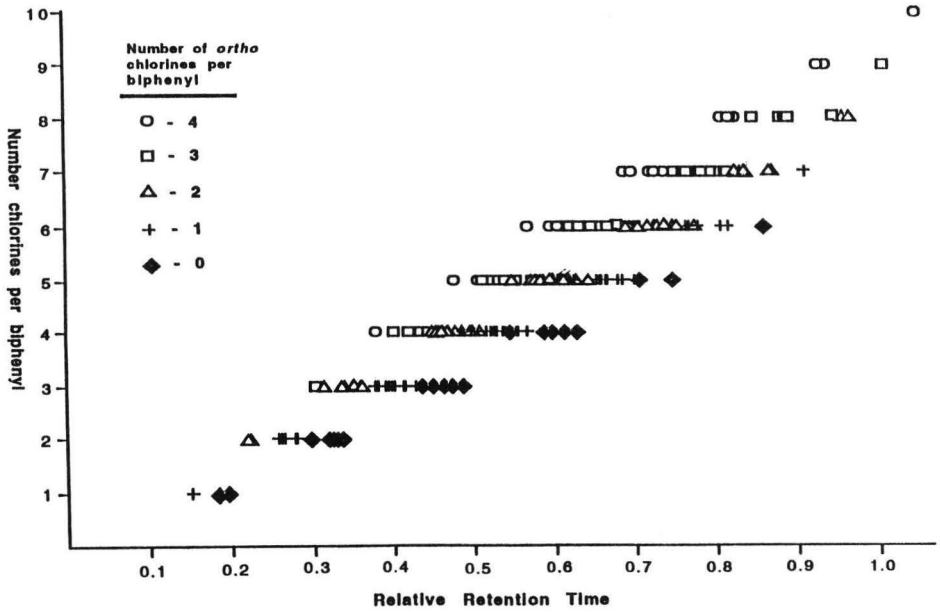


Figure 4 **Structure-activity vapor pressure relationship for PCBs. Lower relative retention time indicates higher vapor pressure. Adapted from Mullin *et al.*, (1984).**

mixture is not observed. With the use of capillary columns, over 40 peaks can be separated. For example, a mixture of 67 molecules can result in 44 individual chormatographic peaks. The double effect of the diversity of PCB physico-chemical characteristics on the evolution of congener importance with time and the difficulties of analytical measurements can lead to misunderstanding.

In addition, the accepted methods for PCB analyses is not standardized from one country to another. For example, in the USA, the total area of all the PCB peaks (in the USA even monochlorobiphenyl is considered a PCB) are quantified relative to an internal standard (octachloronaphthalene) even though the response factors are obviously not at all similar between different PCB congeners. Concentrations are reported as mass PCBs per mass sediment or soil and not as molar concentrations. In France, the PCBs total chromatographic surface area is compared to the surface area of a known mass of a commercial mixture. Of course, if the mixtures are different or the environmental sample has evolved, then the results can be misleading. Concentrations are reported as ppm on a mass basis as the referenced commercial mixture (e.g., Aroclor 1254). In Germany, 6 specific congener standards are used to quantify accurately the respective six chromatogrphic peaks (2,4,4'-trichloro-, 2,5,2',5'-tetrachloro-, 2,4,5,2',5'-pentachloro-, 2,3,4,2',4',5'-hexachloro-, 2,4,5,2',4',5'-hexachloro-, and 2,3,4,5,2',4',5'-heptachloro-biphenyl). The smallest is a trichlorobiphenyl. These six peaks are used for subsequent regulatory decisions. Obviously, changes in the relative importance of these peaks would drastically change the results. Concentrations are also reported on a mass per mass basis. Unfortunately, these methods are also applied to environmental samples, where changes in congener importance can occur as the result of physico-chemical and biological processes. Biological processes are especially troublesome as "new" congeners (those not observed in the original mixture) can be produced.

BIODEGRADATION

PCB have been shown to undergo biodegradation under a variety of conditions in the laboratory and in the environment similar to other chlorinated organics (Abramowicz, 1990; Montgomery, Assaf-Anid, Nies, Anid and Vogel, 1991). Two distinct biological systems capable of degrading PCBs have been identified: anaerobic reductive dechlorination and aerobic oxidation.

Naturally occurring anaerobic bacteria can attack more highly chlorinated PCB congeners. In general, this reductive dechlorination process preferentially removes meta and para chlorine substituents (Figure 5 from Nies, 1993) resulting in lower chlorinated ortho-substituted PCBs. This process has been shown to occur naturally and slowly in the laboratory (Quensen, Tiedje, and Boyd 1988) and in river sediments (Brown and Wagner, 1990) and by phototrophic anaerobes (Montgomery and Vogel, 1992). Studies have demonstrated that the PCB reductive dechlorination activity under anaerobic conditions does not require special adapted microorganisms. Common bacterial co-factors (such as vitamin B12) have been shown to be capable of catalyzing PCB dechlorination (Assaf-Anid, Nies, and Vogel, 1992). The source of hydrogen for replacing the chlorine is dervived biologically from water (Nies and Vogel, 1991). This anaerobic process produces some congeners that are not normally found in commercial mixtures. In addition, as the congeners are partly dechlorinated they produce less response analytically and,

therefore, less chromatographic surface area and, thus, apparently "reduce" the PCB concentration on a mass per mass basis. In fact, even if the molar concentration of all PCBs did not change, the dechlorination would lead to a smaller mass as the chlorine substituent is replaced by a hydrogen. Thus, the same quantity of PCB molecules after partial dechlorination are "reduced" in concentration when expressed as ppm (mg/kg).

Aerobic bacterial degradation of PCBs has been extensively studied. Several microorganisms have been isolated from PCB-contaminated soil demonstrating a preference for degrading lightly chlorinated PCBs (Anid, Ravest-Webster, and Vogel, 1993). Most of these microorganisms attack PCB congeners via the 2,3-dioxygenase pathway to the corresponding chlorobenzoate, which is subsequently degraded by other indigenous bacteria to carbon dioxide, water, and chloride. Aerobic biodegradation has been observed for PCB congeners with up to four chlorine substituents. Naturally occurring aerobic biodegradation has been observed in several cases (Flanagan and May, 1993). Contrary to the anaerobic process, the aerobic process tends to degrade the less chlorinated compounds, specifically the mono- and dichlorobiphenyls (these are not even analyzed by the German method). The result of this degradation is a relative increase of the more chlorinated congeners (since the lightly chlorinated congeners are no longer observed) and possibly some confusion regarding the type of original commercial mixture (i.e., the mixture might appear more heavily chlorinated).

In any case, from a complete treatment viewpoint, a first anaerobic step reducing the chlorine substituents followed by an aerobic step to break up the molecule is required. Natural biodegradation of PCBs does not always occur due to limits in appropriate nutrients or the lack of the proper sequential anaerobic/aerobic processes. Even in the documented cases where natural degradation does occur, the process is very slow (years).

Recently, techniques have been developed to actively bioremediate soils and sediments contaminated by chlorinated compounds (reviewed in Adriaens and Vogel, 1995) including PCBs. The technology for highly chlorinated compounds involves the sequential anaerobic/aerobic processes. The two processes are separated either spatially or temporally. For PCBs, which are not very mobile, the processes are temporally separated (Anid, Nies, and Vogel, 1991). The engineering design can be separated into two parts: anaerobic and aerobic, although consideration of the effect of the anaerobic phase on the subsequent aerobic phase is required.

The first phase requires the induction of active anaerobic conditions if they are not already in evidence as is the case in many soils. This can be acheived by limiting oxygen diffusion from air and by the addition of a harmless suitable simple organic molecule. This compound when degraded by the aerobes present consumes all of the dissolved oxygen, provides energy and carbon for the anaerobes, and has an effect on the subsequent microbial ecology. Significant process performance variations have been linked to different carbon sources (Nies and Vogel, 1990). The correct choice is important, in addition to possible other nutrient requirements. In different in-situ pilot tests, this phase has varied from 5 to 18 months.

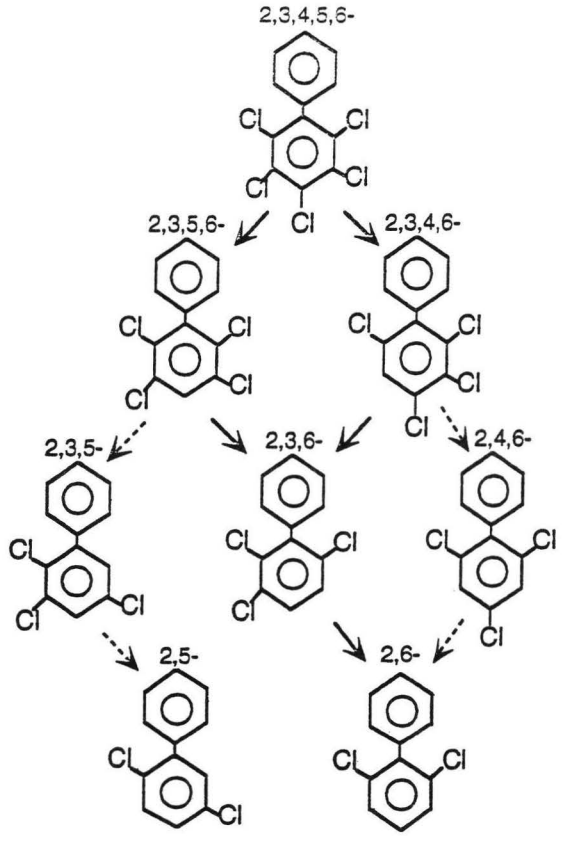


Figure 5 **Proposed dechlorination pathways of 2,3,4,5,6-PCB on CTF sediment. Solid arrows are the major pathways, dashed arrows are the minor pathways.**

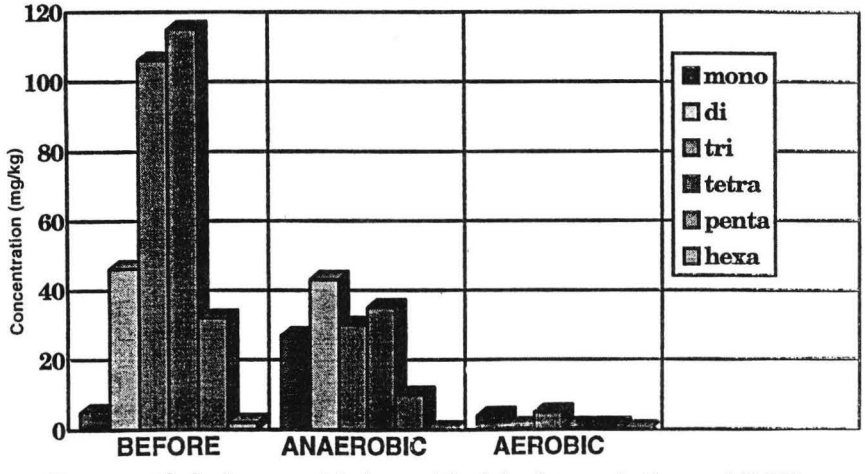


Figure 6 **Sequential Anaerobic/aerobic biodegradation of PCBs**

The second phase requires the induction of aerobic conditions. This can be acheived by various techniques of aeration (Anid, Ravest-Webster, and Vogel, 1993). These techniques need to be in conformity with the rescitation and maintenance of the proper aerobic microorganisms. This process has taken from 2 to 4 months in pilot tests. As in the anaerobic process, only natural indigenous microorganisms are used.

This technology has been applied to both soils and sediments with PCB contamination ranging from 10 to about 500 ppm with no obvious upper limit yet reached. An example of the type of results observed is shown in Figure 6, where the PCB congeners are lumped into isomeric categories in order to observed the degradation trends (mono-, di, trichloro, etc.). The anaerobic phase significantly reduced the PCB concentration and shifted the general pattern to the less chlorinated biphenyls. The subsequent aerobic phase further reduced the PCB total attacking in preference the mono-, di- and trichlorobiphenyls. Often the target degradation levels are set either by limits for putting soil into landfills (below about 100 ppm depending on the local regulations) or leaving the soil in place (less than 10 ppm also depending on the local regulations

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COMPARARTIVE INVESTIGATIONS INTO THE BIOLOGICAL DEGRADATION OF CONTAMINANTS IN FIXED-BED AND SLURRY REACTORS

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Key words: bioreactors, bio-reactor test, bioavailability, biological treatment, carbon balance, contaminated soil, hydrocarbons, microbiological soil remediation, slurry

SUMMARY
To clarify the question whether the slurry process is more efficient than the "dry" process for the biological degradation of contaminants in petroleum contaminated soils comparative balancing investigations were made using laboratory-scale bioreactors. It became apparent that particularly with fresh (not aged) contaminations the contaminant turnover in the fully mixed slurry system is considerably enhanced. This effect is based on an increasing bioavailability of the contaminants due to suspending of and mechanical strain on the soil material in the slurry reactors.

KURZFASSUNG
Zur Klärung der Frage ob durch eine Behandlung im Slurryverfahren der biologische Schadstoffabbau in mineralölkontaminierten Böden gegenüber dem in 'trockenen' Verfahren verbessert werden kann, wurden vergleichende bilanzierende Untersuchungen in Laborbioreaktoren durchgeführt. Dabei zeigte sich, daß insbesondere bei frischen (nicht gealterten) Kontaminationen, der biologische Schadstoffumsatz in den volldurchmischten Slurrysystemen deutlich beschleunigt wird. Dieser Effekt ist auf eine steigende Bioverfügbarkeit der Schadstoffe aufgrund der Suspendierung und mechanischen Beanspruchung des Bodenmaterials in den Slurryreaktoren zurückzuführen.

RÉSUMÉ
Pour répondre à la question s'il est possible d'augmenter la décomposition biologique dans des sols contaminés par du pétrole en appliquant le processus de slurry comparé à des méthodes 'sèches', nous faisions des recherches comparatives de bilan avec des réacteurs laboratoires. On vit bien que particulièrement chez des contaminations fraîches (pas âgées) la décomposition biologique des éléments pollutants était considérablement accélérée dans les systèmes slurry complètement mélangés. Cet éffet se ramenait à la biodisponibilité améliorée des éléments pollutants parce que le matériel de sol était suspendu dans les réacteur slurry et à cause de la contrainte méchanique du sol.

Contaminated Soil '98, Thomas Telford, London, 1998, 531–538

INTRODUCTION

Bioreactors for the biological treatment of contaminated soils are preferably designed as slurry reactors. Their advantage over 'dry' bioreactors consists in an easy management and better process control. They allow to take and evaluate selected actions to increase the bioavailability of the contaminants; on the other hand slurry reactors require a more complicated apparatus and cause higher energy costs.

Within the scope of the research at the DFG-Research Centre SFB 188 "Treatment of Contaminated Soils" comparative investigations into the biological degradation of contaminants (TPH, PAH) in fixed-bed and slurry reactors are carried out at the Department of Waste Management of the Technical University of Hamburg-Harburg. The objective of the investigations was a balancing examination of the conversion processes to assess conversion supporting means and to optimize the biological conversion of contaminants. For this purpose, degradation tests with fixed-bed and slurry reactors were carried out in parallel and the carbon balances of both processes were compared over the course of the tests.

MATERIAL AND METHODS

The investigations were carried out in laboratory bioreactors of 3 litre (fixed-bed reactors) and 4.3 and 12 litre (slurry reactors) volume, applying forced aeration. Figures 1 and 2 show the test systems as well as schematic representation of their system control and data recording.

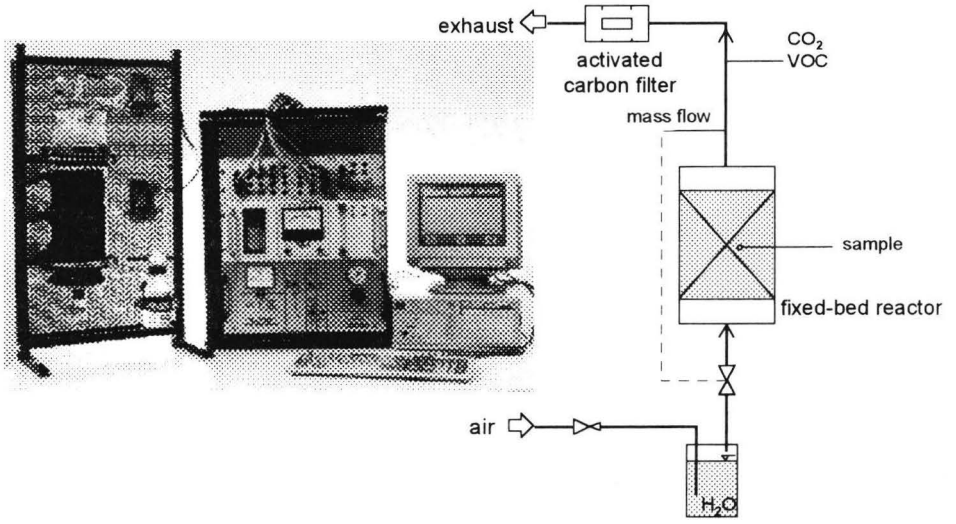
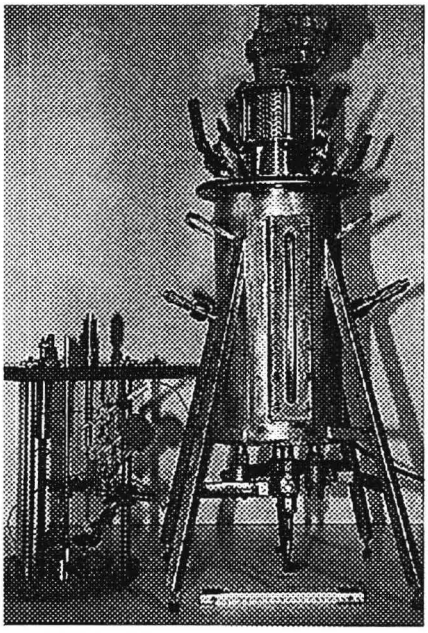


Figure 1: Fixed-bed reactor

The temperature of the fixed-bed and slurry reactors was continuously variable via a heating cable coating. Aeration was effected from the bottom to the top. For all test systems the exhaust gas was examined: the CO_2-concentrations were on-line recorded via infrared photospectrometer and the volatile contaminant components were

discontinuously determined as volatile organic carbon (VOC) by means of a flame ionization detector (FID). Aeration control and exhaust gas data recording were effected by a personal computer. The fixed-bed and slurry reactors were provided with sampling pipes at different heights.



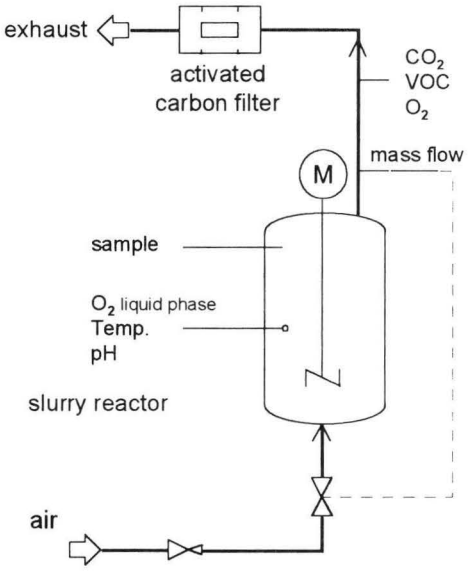


Figure 2: Slurry reactor

When the mixed flow reactors were fully mixed it was possible to keep up to 30% of the solid matter contents continuously suspended by means of agitating tools installed inside the slurry reactors. In addition to the exhaust gas paramaters already mentioned, with the slurry reactors ph-value, temperature as well as O_2-concentrations were on-line recorded during the liquid phase.

To evaluate the biological conversion of contaminants in the reactor systems carbon balances were made according to the balancing approach developed by Stegmann et al., 1991. For the test series using artificially petroleum contaminated soil materials the balance calculation was based on the simplifying assumption that the increased CO_2, VOC and biomass concentrations were caused by the mineral oil addition. Therefore the calculations were made with the difference values between the contaminated and uncontaminated test setups. Although this approach could only describe in part the varying soil conditions after petroleum addition, it provided in a first approximation good indication concerning the conversion of the contamination (Lotter, 1995). In Table 1 the examination parameters and analytical methods for the balancing approach are listed.

Table 1: Measured carbon compartiments and analytical methods

Carbon Compartiment	Analytical Method
Contamination (TPH)	DIN 38409 H18 (modified), GC-FID (Lepom, 1996)
Biomass	SIR-Method (Anderson, Domsch, 1978), protein determination (Lowry et al., 1951)
CO2	on-line: IR ADC DB2E
VOC	discontinuous: TOC-analyser

To obtain fundamental data and to test individual means of optimization, in addition to reactor experiments also investigations into the respiration activity were carried out with the respirometer (Sapromat, Messrs. Voith) at different water contents. For the respirometer investigations and the subsequent reactor tests both really and artificially petroleum contaminated soil materials were used.

RESULTS

PRE-INVESTIGATIONS

As basis of the comparative investigations into the biodegradation of contaminants in fixed-bed and slurry reactors the influence of the water content on the biological activity was examined in respirometer tests in the range of 20 to 30% of the maximum water holding capacity. Figure 3 shows as an example the respiration activity of a soil sample really contaminated with TPH and PAH in dependency of the water content. Below the maximum water holding capacity an area of highest respiration activity develops (50-80% WCmax). At higher water contents the respiration activity decreased. The reason was a limited oxygen supply at water contents in the range of the maximum water holding capacity. Above the maximum water holding capacity sufficient oxygen supply could be ensured by agitating the samples. As a result, respiration activities were observed considerably exceeding those of the 'dry' range. According to Peccia et al, 1997, this increased respiration activity in the water-saturated range is caused by a better bioavailability of the contaminants above the maximum water holding capacity. In addition the solubility of the contaminants is enhanced by the mechanical strain of the soil in the suspension setups (stirring of the samples).

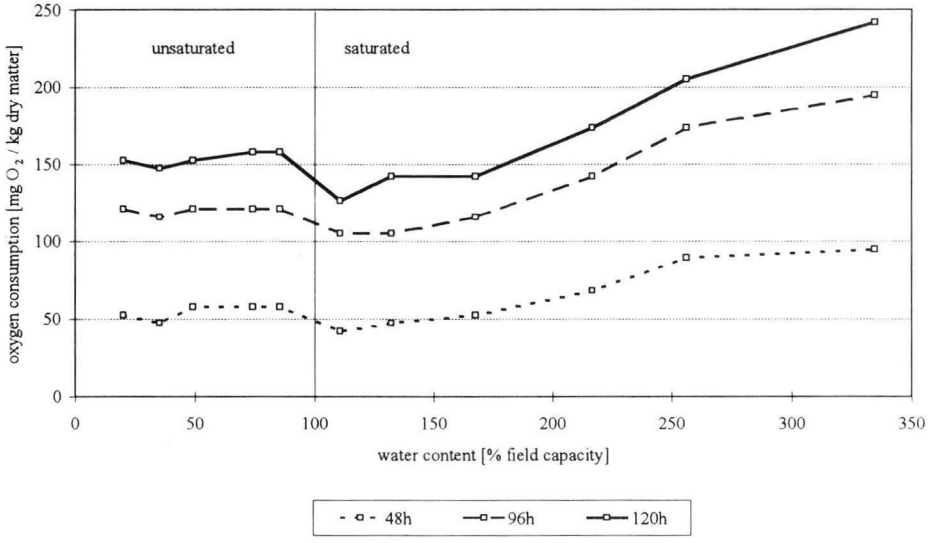


Figure 3: Development of the respiration activity in dependence on the water content

REACTOR TESTS

It could be observed in the tests that due to increasing bioavailability of the

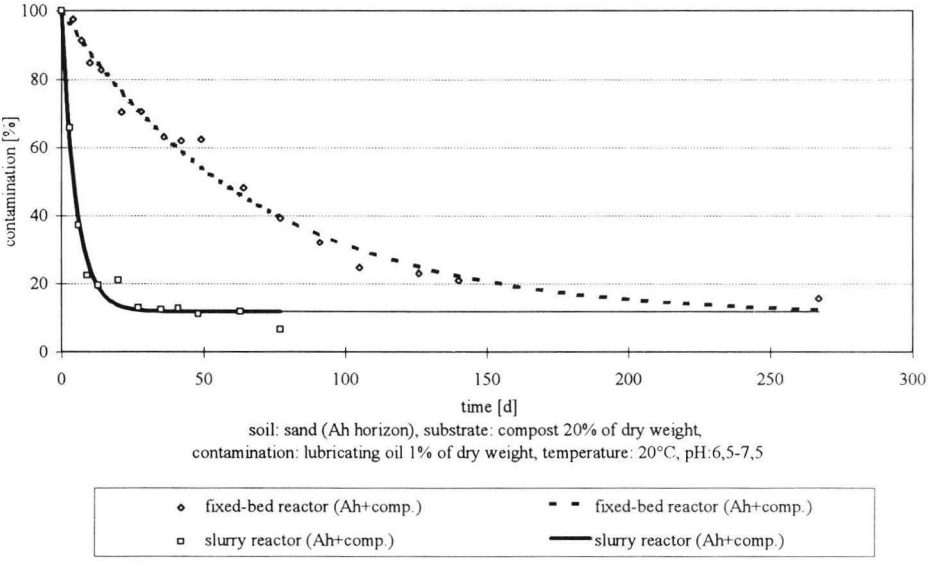


Figure 4: Decrease in the TPH-contents in the fixed-bed and slurry reactors

contaminants in the water-saturated range the contaminant conversion in the slurry reactors was considerably enhanced compared to the fixed-bed reactors (Figure 4).

Figure 4 shows the decrease in the TPH-contents after the biological treatment of a sand of a Ah-horizon artificially contaminated with 1% by weight with lubricating oil for fixed-bed and slurry reactors. As substrate compost (20% by weight) was added to the soil material (Ah+comp). While in the slurry reactor setup already after about 30-day treatment time a stationary plateau phase was reached at approximately 11.5% of the original contamination, this residual contaminant content was obtained in the fixed-bed reactor only after a 270-day treatment time. Thus in the slurry reactor the conversion of the lubricating oil was made about 9 times faster.

When looking at the related carbon balances (Figures 5 and 6) it is observed that only a small portion of the initial contamination (about 15-23%) was mineralized into CO_2 (see also Table 2). In parallel to this balance gaps of up to 80% of the initial contamination occurred. From investigations using ^{14}C labelled tracer substances it can be assumed that these balance gaps are mainly due to the formation of bound residues, which could not be detected with the analytical methods applied in our tests (Kästner et al., 1995). The escape of readily volatile hydrocarbons was negligible both with the fixed-bed and the slurry reactor setups (VOC < 1% of initial contamination). A similar behaviour was found with the contamination concentrations in the liquid phase of the slurry reactors, which were also considerably below 1% of the initial contamination.

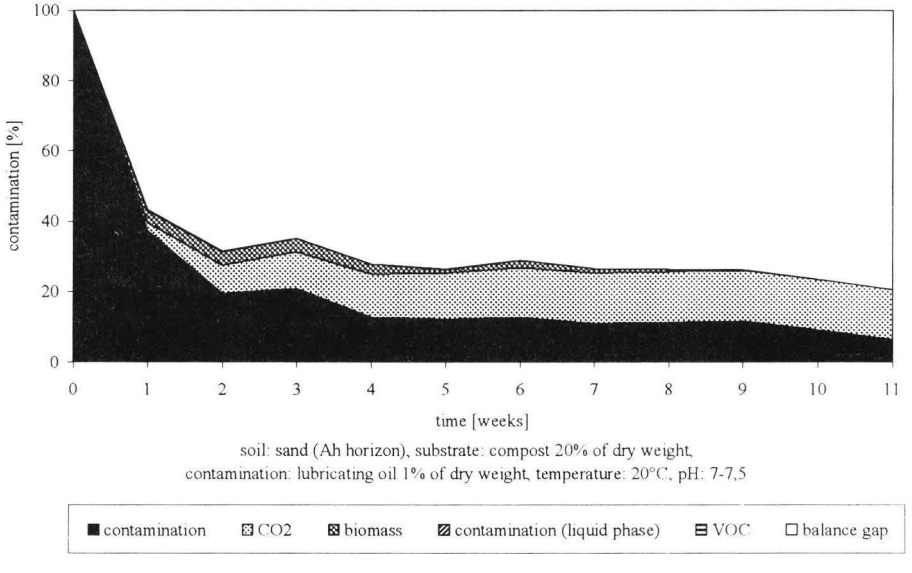


Figure 5: Carbon balance for slurry reactor

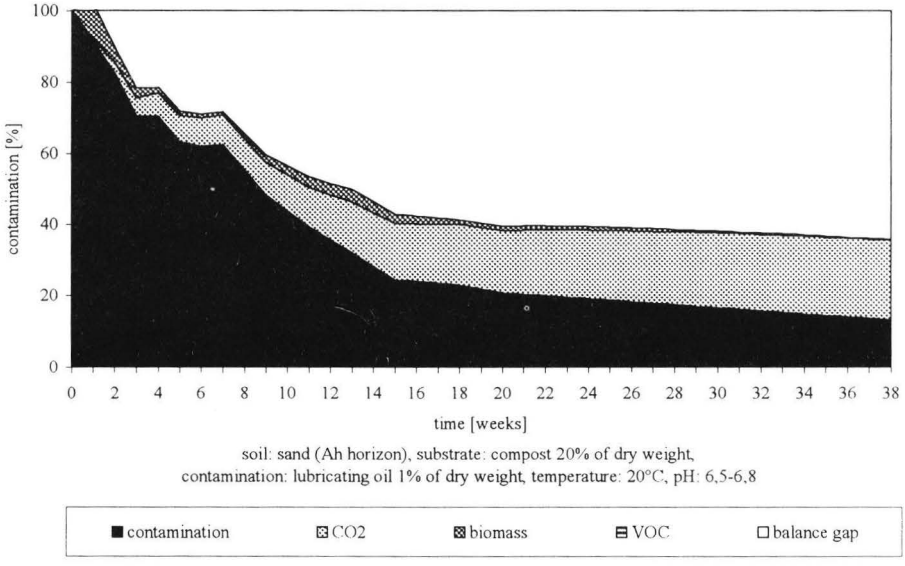


Figure 6: Carbon balance for fixed-bed reactor

Table 2: Mineralization of lubricating oil in the fixed-bed and slurry reactor

Reactor type	Treatment time [d]	Mineralisation [%-contamination]
slurry reactor (Ah+comp.)	77	15,86
fixed-bed reactor (Ah+comp.)	267	22,36

Regarding the conversion processes in the slurry reactor setup over the time it was found that simultaneously with the contaminant decrease at the solid particles and the increasing contaminant concentration in the liquid phase an augmentation of the biomass and a considerable increase of the CO_2-production took place. This finding indicates the role of contaminant solution as a speed-limiting step in the biological contaminant conversion.

Presently within the scope of the research centre "Treatment of Contaminated Soils" a series of actions for advanced contaminant degradation in 'dry' and slurry systems are investigated (e.g. rising the treatment temperature and application of extremely thermophilic microorganisms, process combination: biology-ozonization). Selected results from the current research work will be reported in the oral presentation.

CONCLUSIONS

Due to increased bioavailability of the contaminants during transition from the water-unsaturated to the water-saturated range the microbiological contaminant conversion could be considerably enhanced in the slurry reactor compared to the 'dry' systems. This holds above all for fresh, not aged contaminants, where the contaminant transition from the solid to the liquid phase takes place without additional solubilizers. After completion of the primary contaminant degradation (reaching of the plateau phase) only a minor degradation of the residual contamination takes place. When additional degradation is wanted at this point selected actions must be taken (e.g. ozonization, rise in temperature, use of solubilizers, etc.) In addition the results indicate that by means of slurry tests the expected decontamination success in dry processes can be assessed. The investigations into this problem are currently continued.

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PERFORMANCE CHARACTERISTICS OF A MULTI-STAGE PROCESS FOR EX SITU TREATMENT OF SOLIDS OR LIQUIDS CONTAMINATED WITH CHLORINATED ORGANICS

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Key words: chemical treatment, contaminated soil, dioxins, gas emissions, organic chlorinated compounds, PCB, PCDD/Fs, thermodesorption

SUMMARY

The US Environmental Protection Agency has sought to develop soil decontamination technologies which are effective, but which do not involve incineration. This paper presents the results of a study in which a steam-assisted, thermodesorption system utilized on Guam was characterized in terms of its effectiveness for removing PCBs and PCDD/Fs from soil. Data are also presented which are indicative of the performance of the air pollution control system which is directly coupled to the thermodesorber. The potential for formation of PCDD/Fs during thermodesorption is discussed.

KURZFASSUNG

Die US-Behoerde fuer Umweltschutz hat nach einer Entwicklung einer wirkungsvollen Technologie zur Bodenaufbereitung gesucht, ohne eine Verbrennung des Bodens herbeizufuehren. Der vorliegende Artikel praesentiert die Ergebnisse einer Studie, in der ein dampfunterstuetztes Thermodesorbtionssystem, angewendet auf Guam, auf seine Effektifitaet untersucht wurde, PCBs und PCDD/Fs aus dem Erdreich zu entfernen. Es werden auch Daten vorgestellt, die fuer die Leistung des an den Thermodesorber, unmittelbar angeschlossenen Luftverschmutzungs-Kontrollsystems kennzeichnend sind. Die Moeglichkeit einer Bildung von PCDD/Fs waehrend der Thermosorbtion wird diskutiert.

RESUME

L'Agence Americaine de Protection de l'Environnement (US EPA) cherche a developper des technologies efficaces de decontamination des sols sans incineration. Cet article presente les resultats d'une etude dans laquelle un systeme de thermodesorption assiste par vapeur utilise a Guam est evalue en terme de d'enlevement (removal) des PCBs et PCDD/Fs contenus dans le sol. Des donnees sont aussi presentees et indiquent la performance du systeme de controle de la pollution de l'air. Ce systeme est directement couple a celui de thermodesorption. La possibilite de la formation de PCDD/Fs durant la thermodesorption est discutee.

Contaminated Soil '98, Thomas Telford, London, 1998, 539–548

INTRODUCTION

The United States Environmental Protection Agency's (USEPAs) National Risk Management Research Laboratory (NRMRL) has been involved in developing chemical dechlorination technology for nearly 20 years. Initial efforts focused on developing a process which utilized a reagent consisting of an alkali metal salt of a polyethylene glycol. This process was successfully applied to treat 1-ton batches of soil which was contaminated with several hundred parts-per-million of polychlorinated biphenyls (PCBs)[1]. Subsequently, NRMRL personnel developed and patented another chemical dechlorination process termed Base Catalyzed Decomposition (BCD)[2,3,4]. For treating solids (e.g. soil, sand) the BCD process involves two steps. In the first stage of the process, soil [to which sodium bicarbonate ($NaHCO_3$) has been added in concentrations ranging from 2% to 12% on a weight:weight basis] is fed into a thermodesorption unit. The soil is heated to 340°C. During heating, the $NaHCO_3$ may react with halogenated organics such as chlorophenols and PCBs to form partially or totally dechlorinated organic reaction products, plus inorganic chlorides such as sodium chloride. The $NaHCO_3$ may also assist in breaking up agglomerated soil particles, thus facilitating volatilization of contaminants. The volatilized contaminants and entrained fine particles emanating from the thermodesorption treatment must be captured and subsequently treated in the Second Stage of the BCD Process. In the Second Stage of the BCD process, the collected chlorinated organics are treated using a mixed reagent which includes a base, a hydrogen donor and a catalyst.

In April 1996, the US Navy began utilizing a technology - the Base Catalyzed Decomposition Process (BCDP) - on Guam for treating soil contaminated with polychlorinated biphenyls (PCBs) as well as polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs). This technology is similar to the BCD process developed by the USEPA. The BCDP technology entails heating soil (to which 1% $NaHCO_3$ has been added) to 300°C in a rotary calciner while injecting steam. The volatilized organics and fine particulates produced during the 1-hour thermodesorption are swept into an Air Pollution Control System (APCS) which removes particulates and organics from the flue gas stream prior to venting to the atmosphere. The treated solids from the thermodesorber are returned to the site or deposited in a landfill. The particulates and liquids collected in the APCS must be subjected to further treatment since these materials typically are contaminated with halogenated organic residues including PCDD/Fs. The Second Stage of the BCD process is not presently used in Guam.

It is generally recognized that thermodesorption can remove many types of organics from soil and similar solids (sand, gravel, sediments) and the effectiveness of the BCDP technology for removing PCBs from Guam soil has been reported[5,6]. PCDD/Fs are often found in association with PCBs and these compounds, especially the 2,3,7,8-substituted congeners, have been identified as being particularly toxic. PCDDs and more likely PCDFs can be generated during the manufacture of PCBs; in addition, PCDD/Fs can be formed from PCBs under certain conditions[7,8]. The BCDP system operating on Guam presented an opportunity to not only assess the overall performance of the BCDP system but to obtain data regarding the fate and formation of PCDD/Fs during implementation of the BCDP system. With the cooperation of the US Navy, a plan was formulated for

sampling the various process streams associated with the BCDP unit followed by subsequent analyses of these samples to obtain a more complete understanding of the chemistry of soil-bound PCBs and PCDD/Fs during BCDP treatment.

The study had two objectives:

1. Determine the efficiency of the thermodesorption process for removing PCBs and PCDD/Fs from Guam soil

2. Concurrent with Objective 1, determine the location in the APCS where PCBs and PCDD/Fs are being removed.

In the sections which follow, the BCDP Demonstration Unit located in Guam will be described and the results of the sampling and analysis program will be discussed.

DESCRIPTION OF THE BCDP TECHNOLOGY

The BCDP Demonstration Unit[5,6] includes the Rotary Kiln Reactor (RKR) which is directly coupled with the Air Pollution Control System (APCS). The BCDP unit comprises several modules which are coupled in series. These modules are described below.

Rotary Kiln Reactor System.- The reactor is a rotary calciner consisting of two concentric carbon steel shells. Soil containing 1% sodium bicarbonate is fed into the calciners inner shell at the rate of 900 to 1800 kg per hour. The inside shell rotates and is heated externally to 315°C to 485°C. Steam, at a flow rate of 48 kg/hr., is injected countercurrently to the soil flow. Volatilized organics and entrained particulates are swept into the APCS by the flow of steam and the slight negative pressure created by the in-line blower positioned just prior to the carbon column in the APCS.

Multiclone (MC).- This unit removes particles by centrifugal force and is electrically heated to minimize condensation.

Wet Electrostatic Precipitator (WESP).- Additional steam, at a flow rate of 265 kg/hr, is injected to prevent formation of an explosive mixture. A charged grid imparts electrostatic energy to suspended particles to promote particle agglomeration and precipitation.

Primary Condenser (PC).- This is a shell-and-tube condenser which cools the gases from 100°C to 30°C. The flow of gases entering the condenser is 3.68 cubic meters per minute and, due to condensation, the gas flow leaving the condenser is 0.85 cubic meters per minute.

High Efficiency Mist Eliminator (HEME).- This module consists of a tightly woven fiberglass pad about 7.6 cm thick. The HEME is designed to remove nearly 100% of the particles >3 micrometers and 99% of the <3 micrometer particles.

Carbon Column.- After the HEME, the gas passes through an induced draft fan. The exhaust is routed through a carbon column to remove residual organic vapors, prior to exhausting to the atmosphere.

FIELD SAMPLING AND LABORATORY ANALYSES

The sampling and analysis program was designed to provide data to be used in assessing the performance of the RKR to remove PCBs and PCDD/Fs from the Guam soil, and to determine the location in the APCS where these compounds are being removed. The various process streams which were sampled and the analyses which were performed are discussed in the paragraphs which follow.

Feed Soil (RKRF), Treated Soil (RKRP), Breach Soil, and Cyclone Fines.- The concentrations of PCBs, PCDD/Fs in the feed soil, treated soil and cyclone fines were quantitated using gas chromatographic/mass spectrometric analytical methods [EPA Method 680 for PCBs[9] and EPA Method 8290 for PCDD/Fs[10]]. The concentrations of these compounds in the treated soil were compared to the concentrations of these compounds in the untreated soil to calculate percentage removals achieved during each of three 6-hour tests. During each test, samples of the treated and untreated soil were taken each hour, then composited to obtain a single sample representing the soil before and after treatment during the six-hour test. Similarly, PCBs and PCDD/Fs were quantitated in the cyclone fines. The breach soil is a mixture of feed soil which drops out of the front end of the kiln and cyclone fines which are collected and ultimately recycled back through the process. The concentration of PCBs in the feed soil and in the cyclone fines were quantitated and the ratio of soil to cyclone fines was calculated and utilized to determine the concentrations of PCDD/Fs in the breach soil.

WESP Blow-down, WESP Makeup Water, and Primary Condensate.- Each of these streams was sampled hourly during each 6-hour run and the samples were then composited to obtain one sample for each stream. The composited liquid samples were analyzed by EPA Method 680 for PCBs and EPA Method 8290 for PCDD/Fs. It was necessary to analyze the WESP makeup water because this is recycled process water and contains the analytes of interest. These data, in conjunction with the other data, provided an indication of the performance of the WESP in removing PCBs and PCDD/Fs from the gas stream.

Gas Sample Before HEME and Gas Sample After HEME.- The gas streams entering the HEME and exiting the HEME were simultaneously sampled and the samples subsequently analyzed using the methodology described in USEPA Method 23[11]. Gas sampling was performed throughout the duration of each of the three six-hour runs. PCBs and PCDD/Fs were quantitated using gas chromatographic/mass spectrometric methods. The resulting data were used to calculate the efficiency of the HEME for removing the target compounds from the gas stream.

Rationale for Not Assessing the Performance of the Carbon Column.- The efficiency of the carbon column in the APCS was not assessed due to the fact that stack sampling data were available and funding for the present project was limited.

RESULTS AND DISCUSSION

PCBs and PCDD/Fs in Soil Samples Before and After Thermodesorption

Table 1 lists the concentrations of PCBs, PCDDs, and PCDFs found in feed soil (untreated soil) and treated soil for each of the three tests. It should be noted that the table includes the limits of detection for those cases where no PCBs were found and includes the number of isomers in those cases where PCBs were detected. In some cases, the values in the table

Table 1. Concentrations of PCBs, PCDDs, and PCDFs in Untreated (RKRF) and Treated (RKRP) Soil Samples from Base Catalyzed Decomposition Process Operating on Guam

Date Sample Collected in Guam	Sample Number	PCB Concentration in ppb (nanograms per gram)										Total PCB Concentration (ppb)
		MONO	DI	TRI	TETRA	PENTA	HEXA	HEPTA	OCTA	NONA	DECA	
2/25/97	RKRP-1	RO[1]	10(6)[2]	40(10)	160(18)	480(22)	1300(23)	460(15)	40.0(5)	ND[1.0][3]	ND[2.0]	2400
2/25/97	RKRF-1x	ND[20]	ND[20]	670(4)	2600(8)	21,500(15)	94,000(17)	51,700(15)	9800(9)	280(1)	ND[100]	180,250
2/26/97	RKRP-2	ND[1.0]	2(3)	9(7)	40(13)	240(19)	1400(23)	770(18)	110(9)	2(1)	ND[1.0]	2593
2/26/97	RKRF-2x	ND[20.0]	ND[20.0]	80(1)	3400(8)	61,200(16)	283,000(20) y	164,000(19)	30,100(9)	990(2)	ND[90]	543,000
2/27/97	RKRP-3	ND[1.0]	3.0(3)	20(7)	110(18)	780(24)	3600(24) y	1900(18)	270(9)	7.0(2)	ND[1.0]	6700
2/27/97	RKRF-3x	ND[20]	ND[20]	80(1)	3200(7)	58,700(15)	273,000(21) y	158,000(18)	30,000(9)	820(1)	ND[90]	524,000

Date Sample Collected in Guam	Sample Number	PCDDs Concentration in ppb (nanograms per gram)					Total PCDD Concentration (ppb)
		TETRA	PENTA	HEXA	HEPTA	OCTA	
2/25/97	RKRP-1	ND [1.5]	ND [1.8]	ND [1.8]	ND [2.8]	ND [4.0]	ND
2/25/97	RKRF-1	0.049 (1)	RO	0.44 (4)	1.42 (2)	4.51	6.42
2/26/97	RKRP-2	ND [1.5]	ND [2.3]	ND [1.9]	ND [3.4]	ND [4.7]	ND
2/26/97	RKRF-2	ND [0.02]	ND [0.03]	0.30 (4)	0.81 (2)	2.48	3.58
2/27/97	RKRP-3	ND [3.6]	ND [4.3]	ND [4.0]	ND [5.2]	ND [5.7]	ND
2/27/97	RKRF-3	ND [0.02]	ND [0.03]	0.19 (3)	0.74 (2)	2.27	3.20

Date Sample Collected in Guam	Sample Number	PCDFs Concentration in ppb (nanograms per gram)					Total PCDF Concentration (ppb)
		TETRA	PENTA	HEXA	HEPTA	OCTA	
2/25/97	RKRP-1x	18.6 (3)	RO B	0.83 (1) B	ND [1.7]	ND [3.5]	19.4
2/25/97	RKRF-1	32.4 (14)	21.1 (11)	6.76 (7)	2.03 (4)	1.63	63.9
2/26/97	RKRP-2x	29.9 (4)	21.6 (2)	4.33 (2) B	ND [2.1]	ND [4.1]	55.8
2/26/97	RKRF-2	16.7 (13)	12.9 (11)	5.56 (8)	7.06 (4)	7.05	49.3
2/27/97	RKRP-3x	104 (5)	85.4 (5)	22.9 (3)	ND [3.3]	ND [4.9]	212
2/27/97	RKRF-3	9.64 (16)	9.13 (9)	9.59 (9)	5.07 (3)	5.0	38.4

[1] RO = peak(s) detected but ratio out (indicating ratios of either the M^{+}/M^{+2} peaks or the M^{+2}/M^{+4} peaks fall outside acceptable limits). B = analyte found in blank.
[2] ( ) = No. of isomers observed.
[3] [ ] = detection limit
x - reported data for the sample not recovery corrected
y - concentration of analyte in sample exceeds the upper calibration limit and is therefore considered an estimate

are flagged due to the fact that high concentrations proved difficult to quantitate accurately.

For PCDDs, comparatively low levels of PCDDs are present in the soil before treatment (values range from 3 ppb to 7 ppb) and concentrations were below detection limits after treatment (refer to RKRP values). Detection limits, however, were not much lower than the range of concentrations before treatment.

The concentrations of PCDFs are significantly higher than that of PCDDs in all samples. For example, the PCDFs in the reactor feed (RKRF) ranged from 38 to 64 ppb whereas the PCDDs in the same samples ranged from 3 ppb to 7 ppb. Therefore, the ratio of PCDF to PCDD is approximately 10:1 in the RKRF samples. This is as expected since the Guam soil was contaminated with discarded transformer oil, and PCBs are more likely to be converted to PCDFs than PCDDs during heating of transformer oil.

Concentrations of PCDFs in the treated soil deserve special comment. On February 25, the first day of this testing program, the levels of PCDFs in the treated soil were found to be 30% of the concentration of PCDFs in the before-treatment soil. However, in the second test, PCDF concentrations in the treated soil were approximately equal to the levels in the untreated soil. In the third test, PCDF concentrations in the treated soil were 5.5 times the level of PCDF in the untreated soil. Also, the ratio of concentrations of the tetra-octa congener groups changed during treatment. The concentrations of hepta-octa chlorinated PCDFs decreased and the concentrations of tetra-, penta-, and hexa-congeners generally increases after treatment. These results suggest that PCDFs are formed during treatment using stage 1 of the BCD process, i.e., the thermal treatment stage. This result is not surprising considering the reports in the literature[7,8] which indicate PCBs can give rise to PCDFs especially when air is present, at or near 250°C and up to around 650°C. Air leakage was a problem during these test runs due to worn knife gate valves.

Additional Data

Although a large amount of additional data were obtained, it cannot be included in this paper and will be published elsewhere. Some of the data are summarized in the following table. The International Toxicity Equivalent Values for 2,3,7,8-substituted PCDD/Fs published in 1989[12] were used to calculate Toxicity Equivalent (TEQ) values for feed soil, treated soil, and air samples collected before and after the HEME (and upstream of the final carbon column). These values are shown in Table 2.

Table 2. Toxicity Equivalent Values Calculated on the Basis of PCDD/F Concentrations

Date Sample Collected in Guam	Sample Number	Sample Type	TEQ
25 Feb 97	RKRF-1	Feed soil	3.15 ng/g
25 Feb 97	RKRP-1	Treated soil	1.01 ng/g
25 Feb 97	HEME Outlet	BCDP Exhaust	12.9 ng/m^3
26 Feb 97	RKRF-2	Feed soil	1.75 ng/g
26 Feb 97	RKRP-2	Treated soil	2.02 ng/g
26 Feb 97	HEME Outlet	BCDP Exhaust	1.36 ng/m^3
27 Feb 97	RKRF-3	Feed soil	1.50 ng/g
27 Feb 97	RKRP-3	Treated soil	15.3 ng/g
27 Feb 97	HEME Outlet	BCDP Exhaust	1.72 ng/m^3

The increase in TEQ values for treated soil is due to the increased concentrations of residual PCDFs.

The overall performance of the thermodesorption unit and the APCS are discussed in the section which follows.

Treatment Efficiency of the BCDP Thermodesorption Unit
The performance of the thermodesorption unit of the BCDP during each of the six-hour test runs was characterized by determining the percentage of removal by BCDP treatment of the PCBs, PCDDs, and PCDFs originally present in the Guam soil.

To determine the treatment efficiency, the following formula was developed:

Efficiency of Treatment (lb/hr basis), % = 100 x (Target input in feed soil - target returned) ① Target input

where:

target = total PCBs, PCDDs, PCDFs, or total 2,3,7,8-substituted PCDD/Fs
target returned = amount of target in treated soil + amount of target in breach soil

The BCDP treatment efficiency for PCBs averaged 96 percent for the three six-hour test runs. This means that 96 percent of PCBs initially present in the soil were removed by BCDP treatment.

In the case of PCDDs, however, the available data could not be utilized to calculate treatment efficiencies. This was due to the fact that no PCDDs were detected in the samples of treated soil and the limits of detection for the PCDDs were higher than the concentration of PCDDs found in samples of the feed soil.

The treatment efficiency values calculated for PCDFs and for total 2,3,7,8-substituted isomers were lower than the values for PCBs and these values decreased from run-to-run to the extent that the third run demonstrated that PCDFs were being formed instead of removed (as evidenced by negative treatment efficiency values). The concentration of PCDFs in the treated soil (product) was over five times higher than the level in the feed for the third test run. Since the furan isomers contributed the most to the total 2,3,7,8-PCDD/F values, the total PCDF and total 2,3,7,8-PCDD/F results follow a similar pattern throughout the data.

Control Efficiency of Air Pollution Control System (prior to the Carbon Column)
Table 3 summarizes the control efficiency of the APCS based on the test results. The control efficiency values shown in this table indicate the fraction of the target compounds entering the unit (total PCBs, PCDDs, PCDFs, or total 2,3,7,8-substituted PCDD/Fs) which were removed by that unit of the APCS expressed as a percentage. For example, a 4 percent control efficiency value for total PCBs on 2/25/97 (see top panel of Table 3) indicates that the multi- cyclone removed 4 percent of the total PCBs emitted by the reactor and entering the multi- cyclone during the 6-hour test run. Similarly, on that same day, the WESP removed 24 percent of the total PCBs which were not captured by the multi cyclone and therefore entered into the

Table 3. Summary of Control Efficiency by Pollutant

Total PCBs	Unit Air Pollution Control Efficiency %				Overall Removal
Date	Multi-Cyclone	WESP	Primary Condenser	HEME	
2/25/97	4%	24%	99.9%	72%	99.98%
2/26/97	6%	74%	99.9%	85%	99.995%
2/27/97	3%	84%	99.9%	78%	99.996%
Average	4%	61%	99.9%	78%	99.99%
Total PCDD	**Unit Air Pollution Control Efficiency %**				**Overall Removal**
Date	**Multi-Cyclone**	**WESP**	**Primary Condenser**	**HEME**	
2/25/97	25%	65%	98%	73%	99.7%
2/26/97	34%	99%	60%	97%	99.97%
2/27/97	17%	99%	65%	93%	99.95%
Average	25%	88%	74%	88%	99.9%
Total PCDF	**Unit Air Pollution Control Efficiency %**				**Overall Removal**
Date	**Multi-Cyclone**	**WESP**	**Primary Condenser**	**HEME**	
2/25/97	10%	33%	98%	74%	99.7%
2/26/97	59%	95%	81%	98%	99.98%
2/27/97	24%	99%	79%	97%	99.98%
Average	31%	76%	86%	90%	99.9%
Total 2,3,7,8 PCDD/F	**Unit Air Pollution Control Efficiency %**				**Overall Removal**
Date	**Multi-Cyclone**	**WESP**	**Primary Condenser**	**HEME**	
2/25/97	17%	39%	98%	76%	99.7%
2/26/97	62%	97%	81%	98%	99.99%
2/27/97	28%	99%	79%	97%	99.99%
Average	35%	78%	86%	91%	99.9%

WESP. The total target input to the WESP also included the quantities of targets present in the makeup water. The removal efficiencies shown for each unit of the APCS indicate that except for the multi-cyclone, each unit removes a significant percentage of the target species, with the APCS exhibiting excellent overall control efficiencies. In calculating overall control efficiencies, uncontrolled target emissions from the reactor were compared with HEME outlet emissions.

As stated earlier in this report, the carbon column was not included in this study. Terres et al reported[5,6] that the dioxin/furan stack emissions (expressed as Toxicity Equivalents) were 0.18 ng per cubic meter.

SUMMARY/CONCLUSIONS

The BCDP technology was found to effectively remove PCBs and achieve the clean level of 2 ppm per PCB congener group using the system operating on Guam. The data for PCDD/Fs indicate that PCDFs apparently form under certain conditions. Although this study did not provide definitive data indicating the cause of formation of PCDD/Fs in the third test, published reports indicate that oxygen levels may play a role.

The APCS was found to perform very well and PCDD/Fs were effectively lowered to concentrations which would readily be removed by carbon column technology. The stack emissions were found to fall well within proposed U.S. EPA guidelines.

Clearly there is a need to treat the solids and liquids removed from the exhaust gas stream by the APCS. This latter treatment can probably be accomplished in one of several ways including the patented Second Stage of the BCD process, incineration, landfilling, or other physical/chemical processes.

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REMOVAL OF ORGANOCHLORINE CONTAMINANTS FROM WASTE WATER USING UV LIGHT AND HYPROGEN PEROXIDE.

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Key Words : Aromatic Hydrocarbons, Chemical Treatments, Chlorinated Hydrocarbons, Pesticides, UV Oxidation, Waste Water Treatment.

Summary

Tecnazene (2,3,5,6-tetrachloronitobenzene) an organochlorine pesticide is used to maintain the quality of stored potatoes and is applied to the surface of the potato post harvest. It is released into the waste water stream from potato processing/washing plants in substantial amounts.

Several approaches have been adopted for its removal. The one considered here is based on UV oxidation with and without peroxide. Rapid breakdown of tecnazene is demonstrated in both cases particularly when peroxide is present, yielding a variety of products including chlorinated phenol, dechlorinated nitrobenzene derivatives, nitrite, nitrate, chloride and organic acids, e.g. oxalic, malonic and maleic acids.

Contaminated Soil '98, Thomas Telford, London, 1998, 549–559

1. Introduction

We at Glasgow have a particular interest in the agro food industries particularly with regard to the quality of the produce, its safety and related environmental issues. In this regard pesticides, their residues and metabolites are central to the whole programme. Over the last few years the quality of the product as presented to the consumer has become paramount.

In the case of potatoes for instance many new central processing and washing plants have been constructed resulting in more obvious point sources of pollutants.

Washing plants as well as processing plants release large quantities of wastes in their effluent stream thereby making an impact in the river downstream of these plants. In the case of potato washing plants the main pollutants are suspended solids and pesticides, while in the case of most potato processing plants much organic matter (potato peelings) is also included.

With regard to crop storage, post harvest chemical treatments are of particular concern, i.e. pesticides that are added to the produce either at time of store loading or once the produce is in place in the store.

In the case of potatoes, in order to maintain the quality sprout suppressant chemicals are applied post harvest (Duncan *et al,* 1992).

As the percentage of potatoes destined for the processing sector is very much on the increase as is the pre-pack markets, more and more chemicals are being applied to the stored potato crop in this manner.

Two chemicals in particular are used as post harvest treatments on stored potato tubers to minimize sprouting, chlorpropham and tecnazene. Chlorpropham is employed worldwide and is applied to the potatoes at regular intervals throughout the storage season. It is not unusual to apply up to 0.1 g a.i./Kg potatoes. This would amount to some 100 Kg of chemical in a 1000-2000 tonne store.

As most of the chemical is either loosely attached to the surface of the potato or absorbed in the skin, the amount released on washing and also peeling can be substantial. Most of this will ultimately reach the water course.

Its immediate impact on the river is obvious as the chemical is phytotoxic (an example of a carbamate herbicide) but it does breakdown fairly rapidly releasing 3 chloraniline and isopropanol both of which lack biocidal activity. However, the ultimate fate of the aniline and other metabolites is still a cause for concern and is being further investigated.

Tecnazene, the other chemical used for the purpose of sprout suppression and dry rot control is applied at time of store loading again in about the same amounts as used for chlorpropham (100 mg ai/Kg tubers).

Tecnazene is an example of an organochlorine derivative of nitrobenzene which is not very water soluble but does persist in the environment (water on this occasion) for some time.

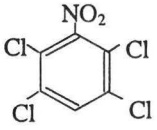
Tecnazene and its metabolites have been identified in sediments and in fish down stream of a potato washing plant (Whale *et al*, 1988).

Determination

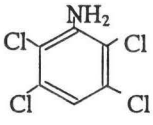
- Tecnazene can be detected at extremely low concentrations, i.e. in the ppb range rather than ppm range.
- Molecules containing 4 chlorine groups are unusual and are easily picked out by GC-MS techniques.

Metabolites

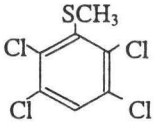
- Tetrachloroaniline (TCA) and tetrachlorothioanisole (TCTA) are major metabolites of tecnazene when decomposed biologically.
- Any residues reported should include these metabolites.



Tecnazene



Tetrachloroaniline(TCA)



Tetrachlorothioanisole(TCTA)

Figure 1. Molecular structure.

Other Background information

- First introduced as a fungicide in 1946.
- Sprout suppressant properties first noted in 1947
- Granules introduced in late 1970's in response to complaints about dusts.
- Use on seed discontinued in 1980's due partly to adverse publicity.
- At the same time potato processors dramatically increased their use of tecnazene.
  1. to delay the onset of chlorpropham induced skinspot.
  2. to overcome early sprouting and wound healing problems.
- Unlike other commercially available post harvest sprout suppressants, tecnazene does not inhibit wound healing and can be used with confidence at time of store filling.
- Generally accepted that tecnazene maintains sprout control and does not 'kill' sprouts.
- In spite of almost 50 years use, the mode of action is completely unknown.
- Use on ware curtailed - consumer driven.
- Effluent problems - residue build up noted.
- Task force set up to supply information requested by PSD (Pesticide Safety Division).

Breakdown

The main metabolites produced microbially both in water, in soil and in fish are the aniline along with the thioanisole (see structures in figure 1.). All three are now determined as routine when tecnazene residue analysis is undertaken (Alchin & Low, 1988).

Lower chlorinated nitrobenzenes have also been detected in fish but not on a regular basis (Yurawecz & Puma, 1983).

Recent claims have mistaken tecnazene for gamma HCH so the problem might be more widespread than originally believed.

The ultimate fate of these metabolites is as yet not determined. Some concern has been registered in this connection. The possibility of the aniline derivative coupling up to give azo derivatives is a distinct possibility in need of much closer examination.

Chemical Destruction

An approach gaining in prominence over the last few years is to us UV light to destroy pesticide residues particularly as a final polishing technique for drinking water. Several attempts have been made to do this with a range of pesticides with variable results. Some interactions with peroxide and ozone and UV light have been studied both with clear as well as cloudy water samples. Again the findings can be somewhat contradictory. On occasion peroxide will aid breakdown, in others the opposite. The same applies in the case of dirty water, sometimes an enhanced breakdown occurs, other times the opposite. Some attempts have been made to account for these anomalies but the situation is still unclear.

What now follows is attempts to look at UV treatment of tecnazene in water with and without the addition of peroxide and to try and identify and quantify the breakdown products formed in an attempt to elucidate the mechanisms of breakdown. Hopefully the findings will be extrapolated to related chemicals in comparable situations with the ultimate aim of coming up with practical recommendations for pesticide removal from these effluent steams.

2. Material and Method

Material

Tecnazene was recrystallised before use. Reagent-grade 30% hydrogen peroxide (BDH Ltd.) was used exclusively. All the organic solvents (Fisher Scientific) used in this study were of HPLC grade. Sodium chloride (Fisher Scientific) and sodium meta-bisulfite (BDH Ltd.) were used as received. The experiments were carried out in deionized and ultrafiltered water.

Experimental

The absorption spectrum of solution

The absorption spectrum of a saturated aqueous solution of tecnazene was measured by ultraviolet spectroscopy.

UV apparatus

1L reactor vessel was used throughout and the contents were stirred using a magnetic stirrer. Irradiation of solution was carried out using an Engelhared Hanovia medium pressure mercury vapour photochemical reactor lamp jacketed with a water cooled quartz sleeve. The lamp emits polychromatic light mainly at $\lambda \geq 254$nm.

Irradiation procedure

Irradiation of 1L of saturated tecnazene solution was carried out. 100ml samples were collected at intervals. In the case of UV irradiation in the presence of hydrogen peroxide, collected samples were transferred to glass bottles containing sodium meta-bisulfite solution which reduces residual hydrogen peroxide immediately. Two different concentrations of hydrogen peroxide, 8.8mM and 88.0mM, were employed. The final concentrations of sodium meta-bisulfite were 0.1mM and 1mM.

Extraction method

The collected 100ml sample was quantitatively transferred into a 250ml separating funnel. A little sodium chloride was added in order to reduce the tendency to emulsify. 10ml hexane was then added and mixed. After allowing the two layers to separate, the hexane layer was removed, and the aqueous phase was then re-extracted with a further 10ml of hexane. The hexane extracts were then bulked, and any water was removed from the hexane by adding anhydrous sodium sulphate. This was then filtered into a 100ml round bottomed flask and evaporated to dryness on a rotary evaporator with water bath at less than 40°C to prevent tecnazene loss. The residue was redissolved in hexane and made up to a final volume of 2ml for GC analysis.

Gas chromatograph

Determination of tecnazene was carried out on a Varian Model 3700 Gas chromatograph instrument equipped with a flame ionization detector (FID). Glass column (1m×0.4cm i.d.) containing 3% O.V17 on a solid support was used.

Study of decomposition products

The solubility of organochlorines, such as tecnazene is very low. As a result of this, the analysis of decomposition products is often difficult to perform due to lower concentrations versus the parent compound. Therefore, acetonitrile was employed on occasion as a cosolvent to increase the concentration of tecnazene in order to obtain greater amount of the parent compound. Acetonitrile was recommended for use as a cosolvent in photochemistry studies (Leifer, 1988), and also was found to have a minimum affect in studies of photodecomposition of pesticides compared to other cosolvents, such as methanol (Bunce, 1978). UV irradiation of 10mg/L tecnazene in 10% acetonitrile solution was carried out in order to identify the decomposition products.

GC-MS

10mg/L in 10% acetonitrile was irradiated for 80 minutes, and then identification of decomposition products in the hexane extracts were carried out on a Hewlett-Packard 5890 Series 2 gas chromatograph interfaced to a 5971 Series Mass Selective detector using a fused silica capillary column (12m×0.2mm i.d.) coated with 0.3µm HP1 Non-polar Methyl Silicone polymer.

Determination of anionic decomposition products

Determination of anionic decomposition products was carried out by analysing water samples containing 10 % acetonitrile treated with UV on a Dionex DX-500 Ion Chromatography equipped with a conductivity detector using a sodium hydroxide gradient to measure ions.

3. Results and Discussion

Solubility of tecnazene

Tecnazene is practically insoluble in water. Leonard (1988) has reported that solubility of tecnazene in water was 0.9mg/L at 20°C. The initial concentration of tecnazene in all of these studies was on average 1.03mg/L which was close to the literature data.

The absorption spectrum of tecnazene aqueous solution

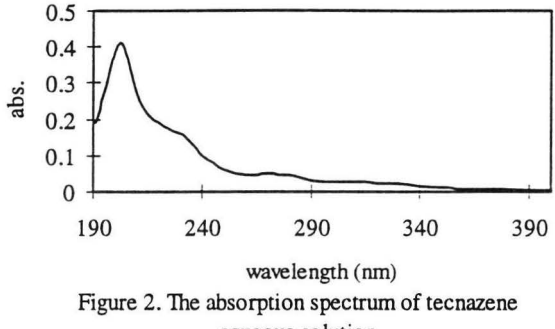


Figure 2. The absorption spectrum of tecnazene aqueous solution

The peak absorption spectrum was at 202.6nm (Figure 2.).

Decomposition by UV with and without hydrogen peroxide

The sample treated with UV in the presence of hydrogen peroxide was decomposed faster than UV alone (Figure 3.). The decomposition rate increased with the increase in the concentration of hydrogen peroxide.

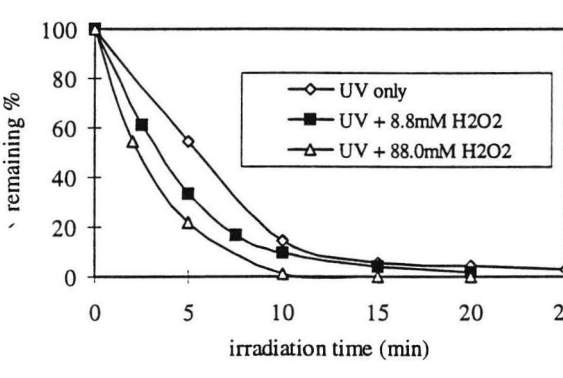


Figure 3. Decomposition of tecnazene using UV with and without H2O2

The reason for different decomposition rates on UV irradiation between samples with and without hydrogen peroxide is that hydroxyl radicals are produced as a consequence of photo-decomposition of hydrogen peroxide (Eqn. 1) (Zwiener *et al*, 1995).

$$H_2O_2 + h\nu = 2 \cdot OH \qquad (1)$$

Hydroxyl radicals are known as the strongest oxidants (+2.85V) in aqueous media apart from fluorine (Scheuer *et al*, 1995). Therefore, in case of UV irradiation in the presence of hydrogen peroxide there are two decomposition processes which are direct and indirect photo-decomposition by hydroxyl radicals.

Study of decomposition products

The decomposition rate in 10% acetonitrile was slower than in water (Figure 4.). The initial concentration of tecnazene in water averaged 1.03mg/L, while in 10% acetonitrile it was 9.99mg/L that was almost 10 times higher than in water. Therefore, different initial concentrations were set up in order to investigate the affect of initial concentration against the decomposition rate. 10% acetonitrile solution was used for both experiments to make conditions the same. The decomposition rate was almost the same as in water when 0.99mg/L tecnazene was irradiated. This result led to the conclusion that the initial concentration of tecnazene is one important factor governing the rate of decomposition (Figure 5.).

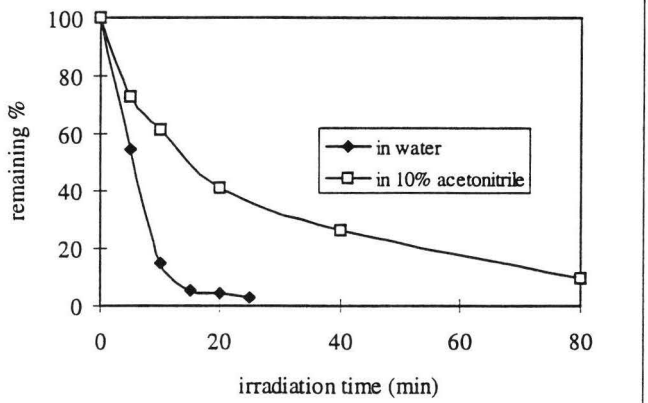


Figure 4. Decomposition of tecnazene with UV

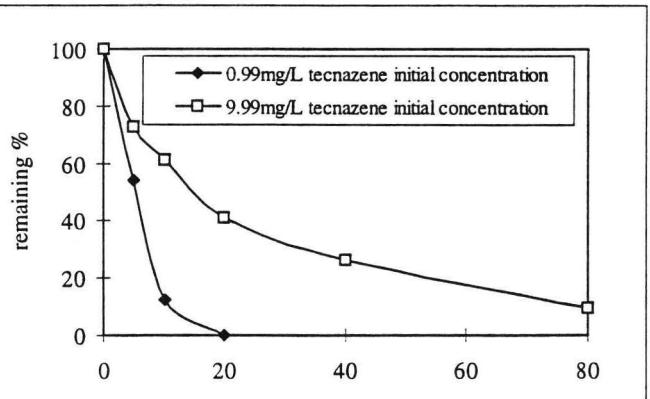


Figure 5. Decomposaition of tecnazene with UV in 10% acetonitrile

GC-MS

After 80 minutes UV irradiation in 10 % acetonitrile, two unknown peaks were determined in hexane extracts by GC-MS (Figure 6.)

The first unknown peak on the chromatogram (RT 9.29 in figure 6.) was identified as trichloronitrobenzene (Figure 7.).

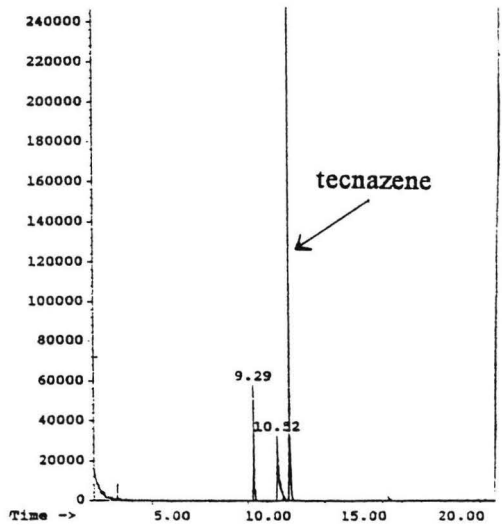


Figure 6. Gas chromatogram.

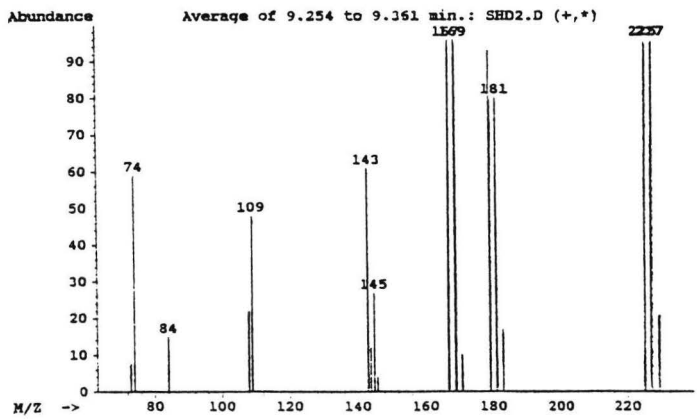


Figure 7. Mass spectra.

The second unknown (RT 10.52 in figure 6.) peak was broad and small. This compound was suspected to be a phenolic compound. Therefore, acetylation with acetic anhydride with pyridine as a catalyst was carried out. As it was shown in figure 8., acetylated compound showed a sharp peak which was identified as acetylated tetrachlorophenol (Figure 9). Hence, one of the decomposition products is tetrachlorophenol.

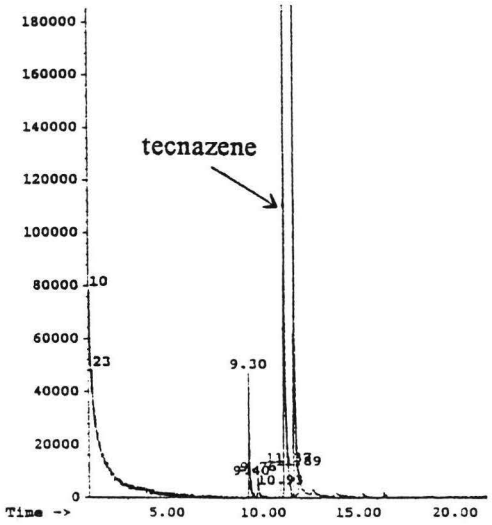


Figure 8. Gas chromatogram (after acetylation).

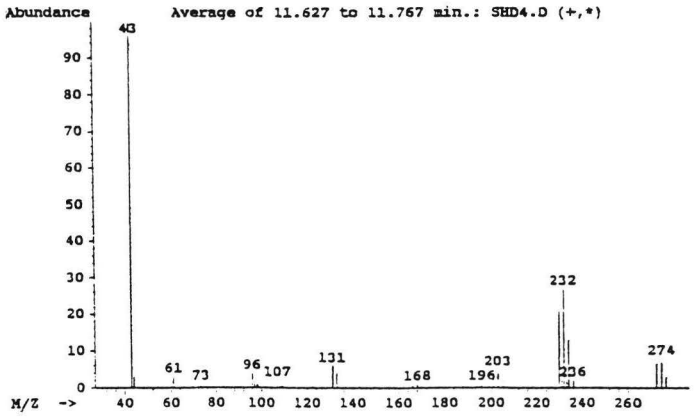


Figure 9. Mass spectra (acetylated).

Determination of anionic decomposition products

Although chloride, nitrate and nitrite were expected as inorganic anionic decomposition products from the structure of tecnazene, acetonitrile itself was found to be decomposed by UV and produced nitrate and nitrite. Therefore, the determination of nitrate and nitrite release was not possible on this occasion. In the case of chloride determination the concentration of chloride increased with decreasing tecnazene concentration (Figure 10.). After 80 minutes irradiation, 90% of the tecnazene was decomposed, and 50% of chlorine from the parent compound was released as the chloride ion at the same time.

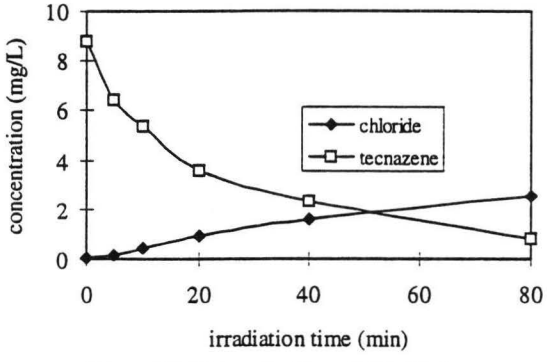


Figure 10. Determination of chloride ion

Extra peaks, suspected to be organic acids, were found on the ion exchange chromatgram of the sample after irradiated for 80 minutes. Oxalic, malonic and maleic were identified with standards.

Various photo-decomposition processes of chlorinated benzenes, such as reductive dechlorination and isomerization were reported by Choudhry et al (1986). In the case of tecnazene, which also has chlorines on the benzene ring, dechlorination was one of the decomposition processes since chloride ion was determined as a decomposition product. Isomers of tecnazene such as 2,3,4,5-tetrochloronitrobenzene were not identified.

4. Conclusions

Our results indicate that hydrogen peroxide is able to accelerate UV photo-decomposition of tecnazene due to the high reactivity of the hydroxyl radical (·OH) species. Hydrogen peroxide works as a photo sensitiser. The decomposition rate increases with increasing concentrations of hydrogen peroxide.

Tetrachlorophenol and trichloronitrobenzene were identified by GC-MS as decomposition products as a result of UV irradiation of tecnazene in 10% acetonitrile. It was also found that rapid dechlorination was one of the decomposition processes when tecnazene was irradiated in 10% acetonitrile.

Obviously much more work is required in this area before the full picture of tecnazene breakdown is revealed and the conversion of the tecnazene to innocuous compounds confirmed. However, supporting results do suggest the presence of organic acids, viz oxalic, malonic and maleic acids as being major end products of the breakdown which should not cause undue concern.

This type of approach (UV plus hydrogen peroxide) does show promise particularly as a compliment to existing practices such as sedimentation and biodegradation. However, the influence of additional components, e.g. the presence of soil, slurry, organic matter, etc. in these reactions will need further investigation before such an approach could be recommended with confidence for commercial situations.

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Resistive heating enhanced soil vapor extraction of chlorinated solvents from trichloroethylene contaminated silty, low permeable soil

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Keywords:
Soil vapor extraction, trichloroethylene, clay, desorption, in-situ remediation, removal rates, temperature, thermal treatment, thermal desorption, volatilization

ABSTRACT

A 2D-laboratory box experiment (12 x 56 x 116 cm) was conducted to simulate the enhancement of soil vapor extraction by the application of low frequency electrical heating (joule heating) for the remediation of a low permeable, silty soil contaminated with trichloroethylene. Joule heating enlarged the flux of extracted TCE with a factor 19 (when boiling) in comparison to the removal rates achieved by soil vapor extraction alone (at 23°C). Within 45 days a removal of 99.8% of the TCE was accomplished.

DEUTSCHE ZUSAMMENFASSUNG

Durchgeführt wurde ein 2D-Laborversuch in einer Kammer (12 x 56 x 116 cm) zur Simulation einer erhöhten Boden-Wasserdampfextraktion. Zweck war die Sanierung schluffigen, mit Trichlorethylen kontaminierten Bodens geringer Durchlässigkeit durch die Anwendung einer Wechselstrom-Niederfrequenz-Erhitzung (Stromerhitzung). Die Stromerhitzung erhöhte den Fluß extrahierten TCEs im Vergleich zu den über reine Wasserdampfextraktion (bei 23 °C) erreichten Extraktionsraten um das 19fache (am Siedepunkt). In 45 Tagen wurden 99,8 % des TCE extrahiert.

RESUME EN FRANÇAIS:

Une expérience de laboratoire en 2D sur un modèle réduit de taille 12x56x116 cm a été mené pour simuler l'amélioration de l'extraction de vapeur du sol par l'application d'un chauffage électrique (résistive) à courant alternative à basse fréquence (chauffage par effet Joule) pour remédier à la faible perméabilité d'un sol silteux contaminé par TCE. L'effet Joule augmente le flux de TCE extrait d'un facteur 19 (en cas d'ébollution) par comparaison les taux d'extraction obtenu par l'extraction de vapeur du sol tout court (à 23°C). En 45 jours 99.8% du TCE a été extrait.

Contaminated Soil '98, Thomas Telford, London, 1998, 561–570

Introduction

Trichloroethylene (TCE) is a halogenated aliphatic compound which has been widely used, as a degreasing agent in the metal industry, on army bases and within the textile industry, for more than 50 years all over the world (Pankow et al., 1996). At present trichloroethylene is one of the most frequently detected halogenated organic compounds in aquifers (Pankow et al.1996). Trichloroethylene is a DNAPL with a density of 1.46 kg/L and a viscosity lower than water (Russell et al. 1992, CRC 1994). Downward migration of spilled TCE is impeded by layers and lenses with higher capillary resistance (in general lower permeability). On top of these layers and lenses TCE pools and spreads out laterally (Pankow et al. 1996, Schwille 1988), leading to deep and complex contaminant spreading throughout the aquifer. At the bottom of the pool TCE slowly enters the low permeable sediment by migration through cracks and by diffusion. The long term presence of these pools on top of low permeable layers and lenses leads to migration of significant amounts of TCE into the low permeable layers.

Based on the potential risks to human health, the drinking water standards for TCE are low (e.g. 5 µg/L US EPA, 1995, 1 µg/L Waterleidingbesluit, 1984). Due to its chemical and physical properties the presence of TCE in the subsurface forms a severe groundwater contamination and a serious threat to the environment, human health and drinking water reserves. Therefore, (rapid) remediation of TCE contaminated sites is required.

A large number of sites contaminated with TCE are located in urban areas or at industrial locations that are still in use. This restricts the accessibility of the sites for remediation of trichloroethylene severely. Consequently, in-situ treatment is most frequently applied. Common applied in-situ remedial technologies, like pump-and-treat and soil vapor extraction (SVE), remove the contaminant from the subsurface with an extraction fluid (liquid or gas) in which TCE is dissolved/partitioned. Subsurface permeability differences lead to preferential flow paths: more permeable zones are flushed significantly more than low permeable zones. Although the permeable zones are swept often and hence remediated relatively fast if no NAPL phase is present, long term remedial actions are common practice. This is caused by the slow release of TCE from the low permeable sediment into the mobile phases. Under natural conditions the contaminant flux generated by diffusion is low, therefore enhancement technologies are needed.

Enhancement of TCE removal by heating of soils

According to Udell (1996), Heron (1997), Davis (1997) and Heron et al. (1998b) the physical mechanisms governing the mobilization of TCE from low permeable soils (solubilization, diffusion, volatilization and sorption) are favorably influenced by increase of temperature. Increase of the soil temperature will lead to a higher flux of TCE to more permeable sediments.

Several methods for the heating of soils are described by Smith & Hinchee (1993), Heron (1997) and Davis (1997). Low frequency electrical (resistive) AC heating (joule heating) is one of the promising technologies for enhanced removal of volatile compounds from clay layers and lenses (Bergsman et al. 1993, Gauglitz et al. 1994, Buettner & Daily 1995, and Phelan et al., 1997). One of the main

advantages of joule heating is its preference for heating high electrically conductive sediments (low permeable clays) over sediments with low electrical conductivity (sands). Joule heating has relatively low heat losses to the more permeable layers, in contrast to steam injection, hot water injection and hot air injection, which primarily heat the clay layers by thermal conduction from the heated permeable zones.

According to Imhoff et al. (1997), Sleep & Ma (1997) and Davis (1997), thermal enhancement of VOC removal is much more effective when used in combination with gaseous phase extraction (SVE) than water extraction (e.g. pump and treat). Therefore the application of joule heating for TCE removal is preferentially conducted in combination with soil vapor extraction. Joule heating in combination with soil vapor extraction was applied in the field (Gauglitz et al., 1994), who showed a significant increase in removal of PCE and TCE from a 3 m thick clay layer and removed more than 99% based on soil cores.

To evaluate the relation between temperature and removal efficiency a laboratory experiment was conducted. This paper describes a two dimensional box-experiment simulating joule heating enhanced remediation of low permeable TCE contaminated soil.

Material and Methods

Box construction

Remediation of a soil section was simulated in a two dimensional test box (56 x 12 x 116 cm inner dimensions). Figure 1 shows the outline of the box. The soil section consisted of a 50 cm thick low permeable layer of silty fine sediment with a thin (10 cm thick) coarse sandy top layer in which the soil vapor extraction system was installed. Next to each electrode a 5 cm thick column of sand was situated to avoid drying of the soil next to the electrodes which would increase the box's resistance extremely. The soil was dry packed in thin layers which were intensively homogenized. After packing the soil, installing all equipment and sealing the box gas tight, CO_2 gas was flushed through the soil for several days to avoid entrapment of air when saturating the soil with spiked (almost TCE-saturated) water through the center inlet in the bottom plate. The average TCE concentration in the inlet water was 1120 mg/L. To avoid entrapment of gas during water addition, the driving force for saturation were the capillary forces; only a slight additional hydraulic head was applied. The total amount of TCE added was 35.5 grams.

The materials used to construct the box were selected on their physical and chemical properties. All materials needed to be resistant to aggressive conditions occurring: high TCE concentrations and temperature variations between 10 and 100°C. Furthermore many components needed to have a low electrical conductivity and low sorption of TCE. The dimensions of the box were determined by the needs to prevent interference of the sides with the electrical conduction and vapor transport, the minimal distance of the electrodes and the height required for simulating soil vapor extraction. The dimensions of the fume hood, in which the box needed to be placed, formed a constraint.

3/4 inch, 18mm, thick Teflon plates were used for the bottom and top. The end plates, 1 cm thick stainless steel, were used as electrodes. For the sides two types of material were used: glass (1 cm) and Teflon (also 1 cm tick). The glass plates were used initially to visualize the wetting of the soil during spiking. After the formation of cracks in the plates due to shear stress when tightening, the box was rebuild with the Teflon sheets.

A support structure was installed to fix the plates and the Viton sealing strips in place. To avoid heat loss, six inches thick of insulation was installed, surrounding the box and its support construction.

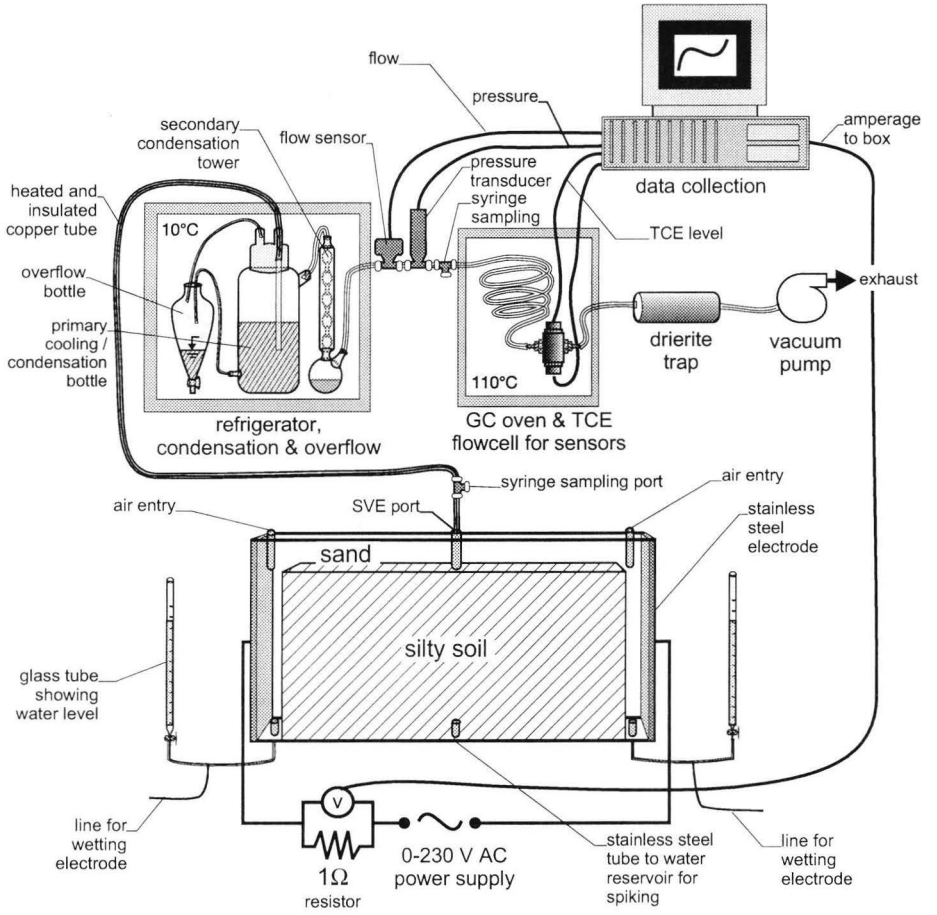

Figure 1 The full setup of the experimental box and vapor treatment

Measurements

Forty-eight thermocouples, with their sensitive tip in the middle of the box, were fixed in the back plate for temperature measurements and electrical conductivity measurements. In the front plate 40 sampling ports were installed for the collection of soil water and/or soil vapor samples for TCE measurements and soil moisture.

Other equipment was installed to control the applied power and the temperature of the electrodes. For a full, more detailed description we refer to Heron et al., 1998a.

The soil vapor extraction system, installed in the top layer, had inlets on each side and a central extraction port. The vapor was extracted with a vacuum pump. The vapor inlets were open to the ambient air. The direction of the vapor flow in the unsaturated zone (the sandy top layer) was from the inlets at the sides towards the central extraction port. The extracted vapor was led through a heated line to a treatment and detection system, consisting of a condensation step, a heating coil and a gas sensing unit with two tin dioxide gas sensors. Before leaving into the exhaust of the fumehood the vapor passed a Drierite trap for final determination of moisture content. The vapor treatment system is described in more detail in Heron et al., (1998c).

Using a LabView controlled data collection system highly frequent (intervals between 1 and 600 seconds) measurements were taken of the extracted vapor (TCE, temperature, pressure and flow rate), the applied power and temperatures in various points.

Frequent (with minimal 4 measuring rounds per day) gas samples of the extracted vapor were collected and directly analyzed on a GC with FID detector, and temperatures were read of a few thermocouples placed in the top and bottom parts of the box.

Less frequently all thermocouples were monitored, electrical resistivities determined and soil vapor and soil liquid samples were collected through all sampling ports and analyzed for TCE.

The vapor flow rate through the sand layer on both sides were determined with a methane tracer test. After completion of the experiment and slow cooling to room temperature, soil samples were taken and analyzed for moisture content and TCE concentration.

Remedial aspects of the experiment

The saturated box was, fully sealed, and left for equilibration for a period of 8 days. Before the start of the soil vapor extraction, a complete sampling of soil fluids for TCE, measurement of the electrical resistivity and temperature was performed. During the experiment five different remedial periods were applied. (1) The first 8 days of the experiment only soil vapor extraction was applied. The temperature in the box was around 23°C. A slight increase of temperature was detected around the outlet, caused by the thermal conduction from the heated vapor extraction line. (2) At day 8, the electrical heating was switched on heating the soil to an average temperature of 85°C reached at day 21. (3) This temperature was kept close to constant, by reducing the applied power, until day 35. (4) Within 4 days the temperature was raised to 99 to 100°C and (5) was kept constant for 5 days after which (at day 45) the power was switched off permanently and the box was cooled down slowly with the insulation still in place.

The application of joule heating is dependent on the soil moisture content and soil conductivity. A low moisture content causes high soil resistance and hence inefficient soil heating, and a high risk of overheating the electrodes. Because

vaporization of water lowered the moisture content, TCE-free water (with the same conductive properties as the water used for spiking) was added during the experiment. A constant hydraulic head was applied. The water was let into the box through two inlet ports at both sides of the bottom in the coarse sand columns.

Results and discussion

The fluxes of extracted TCE in vapor showed significant differences between the five applied soil vapor extraction periods. Figure 2 shows the mass of TCE extracted by the soil vapor extraction system and the soil temperature in the bottom center. The mass of extracted TCE is based on the interpolation of the GC analyses in combination with the data from the gas sensors, the vapor pressure and vapor flow measurements.

The results show that after the extraction of the initial TCE from the vadose zone, a constant TCE-flux of about 0.13 mg/day was extracted by the vapor extraction system at an average soil temperature of 23°C. The predicted duration of a full remediation of the soil based on this flux (not including a decrease of the flux over time) is minimal 270 days. In comparison, when the heating was switched on, and the box heated up with 4.8°C per day, the TCE-flux increased dramatically. Likewise, when the applied power was decreased to maintain a stable soil temperature the TCE-fluxes decreased.

During the two weeks when the temperatures were around 85°C the TCE-fluxes reached an average of 0.35 grams TCE per day (i.e. 3 times the extraction rates at 23°C). At day 35, just before the applied power was increased again, the total extracted mass of TCE was about 20 grams: a little over 40% of the initial added TCE still remained in the soil.

The rising temperature, during the 34th to 39th day, coincided with higher TCE-fluxes detected in the extracted vapors. After reaching boiling temperatures (99 to 100°C) in the box, the TCE-fluxes in the effluent fluctuated significantly over time, at an average rate of 2.5 g/d (i.e.19 times the TCE flux at 23°C).

Subsequently by reducing the temperature below boiling point by switching off the power, the detected TCE-fluxes diminished rapidly below detection limits within days.

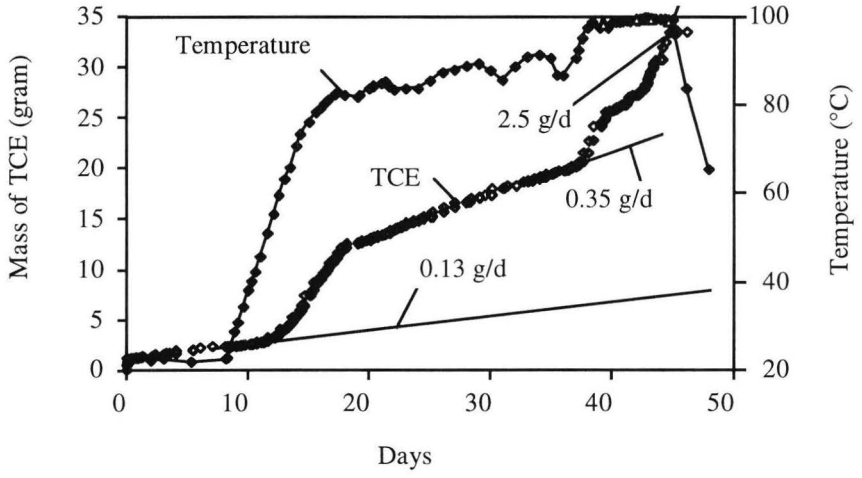

Figure 2 The mass of extracte TCE and the temperature in the bottom center

Analyses of the soil moisture samples and soil samples, collected after a two weeks period of cooling, indicated that even in the bottom center, TCE concentrations in soil and pore water decreased by 2 orders of magnitude, leading to concentrations below the soil criterion (5 mg/kg in Denmark). A total TCE mass of 70 mg remained in the soil after treatment. A removal of 99.8% of the total added TCE within 45 days was accomplished.

Based on the results over 94% of the total removed TCE mass was extracted by the SVE system. These results show the high effectiveness of joule heating, as a supplement to SVE in the permeable zones, to enhance significantlystrongly the cleansing of low permeable, clay/silt, layers which most remedial method fail to address.

Furthermore, the results demonstrate significantly higher removal rates for TCE when temperatures reached boiling point compared to temperature slightly below boiling. This suggests that steam formation and/or the volume expansion in every pore leads to very rapid removal of high concentrations of TCE in tight, almost saturated silt. Therefore, it appears that steam formation is essential for fast removal of volatile contaminants from low permeable soils.

The extraction of steam does however lead to drying of the soil. Since, Joule heating depends on the presence of groundwater for electrical conductance, additional water is required, especially around the electrodes, to maintain conductance.

With regard to the cost of thermal techniques, field applications of thermal techniques have been shown to be economically attractive due to the short treatment times needed for complete contaminant removal (Newmark & Aines, 1997, Bremser & Booth, 1996). In the 2D experiment the relevant aspects for field applications were revealed and related well to initial field tests (Bergsman et al.

1993; Gauglitz et al. 1994, Buettner & Daily, 1995). So was shown the importance of electrode wetting and moisture control to maintain high conductivity and vapor production. Furthermore, good control of the power input in relation to desired in-situ temperatures is essential. The high removal rates achieved in almost saturated soil indicates that large desaturation is not needed for effective remediation.

Although no DNAPLs were present in the remediation experiment and could be in field cases, DNAPL-pools on top of a low permeable layers does not seem to hold back effective soil remediation with the applied technology. On-going research strongly indicates that thermal techniques are even more efficient when NAPL phases are present, since NAPL areas boil preferentially at lower temperatures than 100 °C (Udell, 1996, 1997, Heron et al. 1998d).

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DEMONSTRATION OF ACCELERATED ANAEROBIC BIOREMEDIATION FOR TRICHLOROETHENE (TCE)-CONTAMINATED GROUNDWATER AT DOVER AIR FORCE BASE.

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Keywords: aquifer, bioremediation, case history, chlorinated hydrocarbons, field test, groundwater clean-up, groundwater remediation, halogenated hydrocarbons, in-situ bioremediation, trichloroethylene

SUMMARY

This paper describes the successful application of accelerated anaerobic bioremediation with bioaugmentation to completely degrade trichloroethene (TCE) to ethene in a contaminated aquifer. Using lactate as the growth substrate, the indigenous population was capable of degrading TCE to *cis*-1,2-dichloroethene (DCE). Further degradation of DCE to ethene occurred only after bioaugmentation which was successfully undertaken in the field.

KURZFASSUNG

Das Referat beschreibt die erfolgreiche Anwendung von beschleunigter, anärober Bioremediation unter Bioaugmentation zur völligen Zersetzung von Trichlorethen (TCE) zu Ethen in einem kontaminierten Grundwasserleiter. Unter Verwendung von Laktat als Wachstumssubstrat war die einheimische Bevölkerung in der Lage TCE in cis-1,2,-Dichlorethen (DCE) zu zersetzen. Eine weitere Zersetzung von DCE zu Ethen trat nur nach Bioaugmentation ein, was im Feld erfolgreich durchgeführt wurde.

RÉSUMÉ

Ce document décrit l'application, avec succès, d'une bioréhabilitation anaérobie accélérée avec inoculation, dans le but d'assurer une dégradation totale du trichloroéthylène (TCE) en éthylène, dans une nappe aquifère polluée. En présence de lactate utilisé comme milieu de croissance, la population indigène s'est avérée capable de dégrader le TCE en *cis*-1,2-dichloroéthylène (DCE). La dégradation additionnelle du DCE pour produire de l'éthylène n'a eu lieu qu'après inoculation ; cette opération a été effectuée avec succès sur le terrain.

Contaminated Soil '98, Thomas Telford, London, 1998, 571–574

INTRODUCTION

The Remediation Technologies Development Forum (RTDF) is a consortium of members from industry, government agencies, and academia who share the common goal of developing effective, less costly hazardous waste characterisation and treatment technologies. This is achieved by implementing collaborative research to address identified high priority development needs and the scientific, institutional, and regulatory barriers to their application.

The Bioremediation of Chlorinated Solvents Consortium is one of the RTDF's self-managed Action Teams. It's mission is to accelerate the development of cost-effective bioremediation processes for chlorinated solvents and to achieve public and regulatory acceptance that these processes are safe and effective. To accomplish this, a comprehensive research plan to field-test and evaluate the effectiveness of three *in situ* bioremediation processes for degrading chlorinated solvents (cometabolic bioventing, natural attenuation, and accelerated anaerobic bioremediation) has been established.

This presentation describes the Consortium's field test of accelerated anaerobic bioremediation for chlorinated solvents in groundwater at Dover Air Force Base (AFB), Delaware, USA. The project has included the successful field-scale application of bioaugmentation to completely degrade trichloroethene (TCE) to ethene.

DESCRIPTION OF FIELD SITE

Dover Air Force Base (AFB), Delaware, USA contains several areas of soil and groundwater contaminated with chlorinated solvents and/or petroleum hydrocarbons which have been made available for remedial technology research and evaluation. These projects include the accelerated anaerobic bioremediation test facility.

The surficial geology of the test site comprises glaciofulvial sediments of the Columbia formation underlain at approximately 15 m b.g. by clay of the Calvert formation which functions as an effective aquiclude. In the area of the test cell, the Columbia sediments are predominantly sandy and act as one unconfined aquifer with the water table at 3-4 m b.g. The deep zone of the aquifer, which is slightly more permeable than the upper zone and contains most of the contamination, was used in this project.

The only contaminants present in the groundwater in this area are chlorinated ethenes. Trichloroethene (TCE) is the main contaminant (typical concentration = 10000-20000 µg/l) with *cis*-1,2-dichloroethene (DCE) also present at significant concentrations (1000-2000 µg/l). Tetrachloroethene (perchloroethylene; PCE) and vinyl chloride (VC) are present only at trace concentrations (<50 µg/l).

PROCESS DESIGN

Extensive microcosm studies were performed to investigate the potential for anaerobic biodegradation of chlorinated solvents in groundwater at the test site and to determine potential field operating conditions. Based on the results of laboratory microcosm studies and groundwater flow modelling, the pilot accelerated anaerobic bioremediation test facility was designed as a semi-contained recirculating ground water containment cell. The cell consisted of three downstream extraction wells for groundwater recovery and three upstream injection wells for re-infiltration of groundwater supplemented with lactate and inorganic nutrients. In and around this flow field were located numerous piezometers for groundwater sampling.

The facility was constructed in July-August 1996 and started-up in September 1996.

INITIAL FIELD OPERATING EXPERIENCE

Stoichiometric conversion of TCE to *cis*-1,2-DCE occurred after a lag period but no further degradation of DCE to VC or ethene could be demonstrated. It was concluded that the intrinsic microbial population in this location was not capable of further reductive dechlorination of DCE under the prevailing *in situ* conditions. The decision was therefore made to investigate the possibility of bioaugmentation to initiate DCE degradation.

BIOAUGMENTATION

Following evaluation of cultures available to the Consortium, a mixed dechlorinating population isolated from Pinellas, Florida was selected for further investigation. This is an oxygen-tolerant methanogenic consortium capable of rapid reductive dechlorination of TCE, DCE and VC to ethene (DeWeerd *et al.*, 1998). Laboratory column testing demonstrated rapid and stable dechlorination of accumulated DCE in Dover sediment following inoculation with this culture.

Following regulatory approval, inoculation of the field test cell was performed on two occasions in June 1997. Following a lag period of approximately two months, degradation of accumulated DCE to VC and ethene began and activity has continued to be stable up to the time of preparation of this abstract.

Further investigations are in progress to complete contaminant mass balances across the test cell under pseudo-steady state degradation conditions. Further microbiological testing, with particular emphasis on 16s rRNA characterisation, is proposed to confirm that the degradative organisms are derived from the Pinellas inoculum and to determine which members of the microbial consortium are responsible for the activity.

CONCLUSIONS

A detailed laboratory and field testing programme has demonstrated effective remediation of a TCE plume by engineered accelerated anaerobic bioremediation using lactate as the growth substrate. At the field test cell location at Dover Air Force base, biodegradation of TCE to *cis*-1,2-DCE could be achieved by the indigenous population

once suitable redox conditions had been established but degradation beyond DCE required bioaugmentation which was successfully achieved in the field.

The decision to bioaugment and the execution of this were based on detailed scientific investigation in the laboratory and field. It is not intended that this case be interpreted to mean that inoculation will be generally advantageous at other locations and further data are being obtained at Dover to extend the findings to date and evaluate the role of bioaugmentation.

ACKNOWLEDGEMENTS

The work described in this paper is a collaborative project by the RTDF Bioremediation of Chlorinated Solvents Consortium. The input of all members of the Consortium is acknowledged and the authors would like to express particular thanks to the following individuals: Angelo Bracco, Mike Brennan (General Electric); Skip Chamberlain, Don Maiers, Jef Walker (US Dept. of Energy); Dave Major, Leo Lehmicke (Beak International); Lisa Carmichael (Novartis); Bob West, Nancy Klier (Dow Chemical); Tom Ei. (DuPont); Charles Mikula, Milton Beck (Dover AFB); Jerry Coyle, John O'Reilly, Robert Orth, Kathy Carr (Monsanto); Malcolm Watts, Dave Gannon, Neil Gray , Lori Moser (Zeneca); Greg Sayles, John Wilson, Don Kampbell (US EPA); Dick Woodworth, Cathy Vogel (US Air Force Research Laboratory's Airbase and Environmental Technology Division); Tony Palumbo (Oak Ridge National Laboratory); Sue Pfiffner (Oak Ridge Institute for Science and Technology); Brian Hooker, Rod Skeen (Battelle Pacific Northwest Laboratory); Dave Stahl (Northwestern University).

Particular thanks are due to Dover Air Force Base, Delaware for hosting the field test.

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REMOVING VOLATILE AND SEMI-VOLATILE CONTAMINANTS FROM THE UNSATURATED ZONE BY INJECTION OF A STEAM/AIR-MIXTURE

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Key words: In-situ remediation, large-scale experimental basin, aromatic hydrocarbon contamination, temperature, unsaturated zone, soil vapor extraction (SVE), steam stripping, clean-up technologies

SUMMARY

Soil vapor extraction as a method for removal of non-aqueous phase liquids from the unsaturated zone can lead to extended remediation times. In previous experiments steam injection was successfully applied to increase recovery rates and decrease remediation times. However, steam injection can result in contaminant mobilization at the condensation front and downward migration towards the saturated zone. To avoid downward migration, experiments were conducted on a large scale utilizing the injection of steam/air-mixtures. Results were compared to those of a previous pure steam injection experiment. Clean-up levels were excellent and downward migration was successfully prevented.

KURZFASSUNG

Das Verfahren der Bodenluftabsaugung kann bei Reinigung der mit organischen Chemikalien verschmutzten ungesättigten Bodenzone zu langen Sanierungszeiten führen. In vorangegangenen Experimenten konnte mittels Dampfinjektion der Massenaustrag beschleunigt und Sanierungszeiten erheblich verkürzt werden. Dampfinjektion kann jedoch zu einer Schadstoffmobilisierung in der Wärmefront und einem Absinken flüssiger Schadstoffphase in Richtung gesättigter Zone führen. Um das Absinken zu vermeiden, wurden großskalige Experimente durchgeführt, bei denen Dampf/Luft-Gemische injiziert wurden. Ergebnisse wurden mit denen reiner Dampfinjektion verglichen. Reinigungsgrade waren hervorragend und das Absinken flüssigen Schadstoffes wurde erfolgreich verhindert.

RÉSUMÉ

La méthode d'aération de la zone non saturé pour la dépollution de contaminant NAPL's sur site peut exiger une longue période de fonctionnement. Des essais précédents ont montré que l'injection de vapeur peut accélérer l'extraction de masse et la période de fonctionnement peut être abrégé. Cependant, l'injection de vapeur peut provoquer une mobilisation de contaminant dans le front de vapeur et avec cela une descente de NAPL vers la zone saturé. Afin d'éviter cette descente, des essais à l'échelle technique étaient effectués pendant lesquelles un mélange air/vapeur était injecté. Les résultats était comparé avec ceux de l'injection de vapeur pure. Le degré de décontamination était éminent et la descente de NAPL était évité avec succès.

Contaminated Soil '98, Thomas Telford, London, 1998, 575–584

INTRODUCTION

In recent years subsurface contamination by Non-Aqueous Phase Liquids (NAPLs) such as petroleum hydrocarbons or chlorinated solvents has become a significant environmental concern. Soil Vapor Extraction (SVE) is a common in-situ remediation technology for volatile organic chemicals in the unsaturated zone. Using conventional SVE, remediation times are often prolonged beyond expected durations due to low contaminant vapor pressures or preferential flow causing low contaminant concentrations in the extracted gas (McClellan and Gillham, 1992).

Steam injection was introduced as an effective method for heating the soil and thus increasing contaminant vapor pressure (Udell and Stewart, 1989). Recovery rates of the contaminant were greatly increased and remediation times were decreased. However, steam injection causes a contaminant condensation front. If saturation levels in the front increase beyond residual, the contaminant mobilizes down to the water table (Betz *et al.*, 1997). LNAPLs pool on the water surface and can mobilize outside the containment area. DNAPLs can flow downwards through the saturated zone until retained by a less permeable layer.

To avoid excess condensation and hence downward migration of the contaminant, the gradient of the heat front must be moderated. An innovative remediation method is presented where instead of pure steam a steam/air-mixture is injected into the subsurface. A steam/air-mixture allows for maximum heat transfer but with controllable temperatures to reduce the heat front gradient. A large-scale, three-dimensional, steam/air experiment was conducted in the Research Facility for Subsurface Remediation (*VEGAS*) at the University of Stuttgart (Kobus *et al.*, 1996). The behaviour of the heat front and contaminant recovery were compared to a previous pure steam injection experiment conducted at the same facilities (Betz *et al.*, 1997).

PHYSICAL PROCESSES

When steam is injected into cold porous media it condenses and transfers the heat of vaporization to the sand. The steam can only propagate when the media reaches steam temperature (100°C at atmospheric pressure). The velocity of the heat front is directly proportional to the injected enthalpy flux. The mechanics of steam propagation create steep and stable heat fronts (Färber, 1997).

The heat flux ($\dot{Q}$, kW) required to heat a specific volume (V) of porous medium over time (t) is expressed as:

$$\dot{Q} = \rho_S \, c_{p,S} \, (1-n) \, \Delta T \cdot \frac{dV}{dt} \qquad (1)$$

where ρ_s=2650 kg·m^{-3}, $c_{p,s}$=0.84 kJ·kg^{-1}·K^{-1} and n=0.35 are the particle density, specific heat capacity and porosity of the sand respectively. ΔT represents the temperature difference between the initial cold sand to the final heated temperature. 33 kWh of energy is required to heat 1m^3 of sand to the temperature of steam (20°C to 100°C).

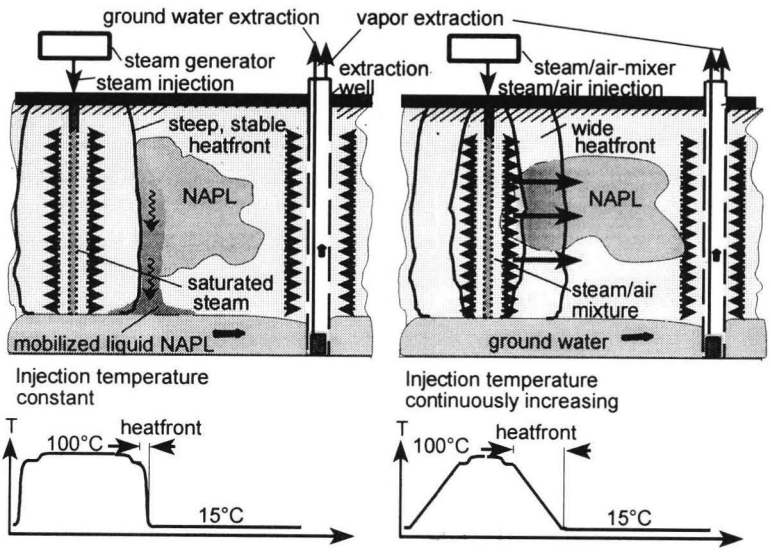
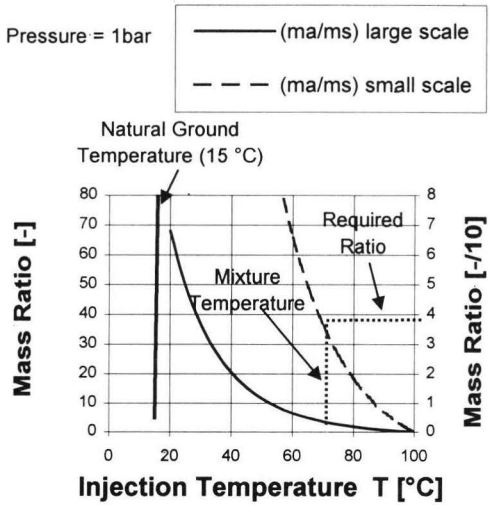


Fig. 1: Contaminant behaviour (schematic) and temperature profile during pure steam injection (left) and injection of a steam/air-mixture (right).



As the heat front moves through the system, contaminants will be vaporized and transported with the flowing gas phase. At the leading edge of the sharp heat front the contaminants come in contact with the cold soil and condense again. This may result in a NAPL saturation above residual and subsequent downward migration of the liquid NAPL. Therefore most of the contaminant leaves the system as a liquid removed from the water surface (Fig. 1, left).

Fig. 2: The thermodynamic behaviour of steam/air-mixtures. Two variations of the same curve, the smaller scale (2nd y-axis) allows greater accuracy in determining the air/steam ratios under 10:1.

The physical processes of heat transfer during steam/air injection are similar to those during pure steam injection. Condensation of the steam component of the mixture is the main heat transfer mechanism to the soil. However, a steam/air-mixture allows the manipulation of injection temperatures to those less than steam.

The injection temperature depends on the mass ratio between steam (ms) and air (ma) in fully saturated conditions. To obtain a certain temperature of injection the ratio of steam to air can be found using Fig. 2. For example, to reach an injection temperature of 70°C, the ratio of steam to air must be 1:3.5. By gradually increasing the injection temperature to steam temperature, the gradient of the heat front can be controlled and a spatially extended, moderate gradient heat front can be created.

During the injection of steam/air-mixtures, the temperature of the porous media and the pore fluids increases to injection temperature. The vapor pressure of the contaminant is increased accordingly and more contaminant is volatilized. Contaminants are transported with the gas flow to the heat front. The spatially extended heat front allows the contaminant to condense in a larger porous volume. Simultaneous SVE constantly removes the contaminant from the heat front zone. As soil temperatures rise, more contaminant is volatilized and thus extracted by SVE. The constant removal of contaminant and the larger condensation area reduce the chance of contaminant levels exceeding the residual saturation of the soil. Contaminant will then migrate as a gas to the extraction well avoiding downward flow (Fig. 1, right).

EXPERIMENTAL SETUP

The experiment was conducted in the 6 m x 6 m x 4.5 m *VEGAS*-container filled homogeneously with sand and sealed with a HDPE cap. Underneath the cap there was a 3.7 m thick unsaturated zone overlying a 0.8 m groundwater zone. A central extraction well was surrounded by six injection wells (Fig. 3). Steam was generated using a 50 kW steam generator and then mixed with air before entering the wells.

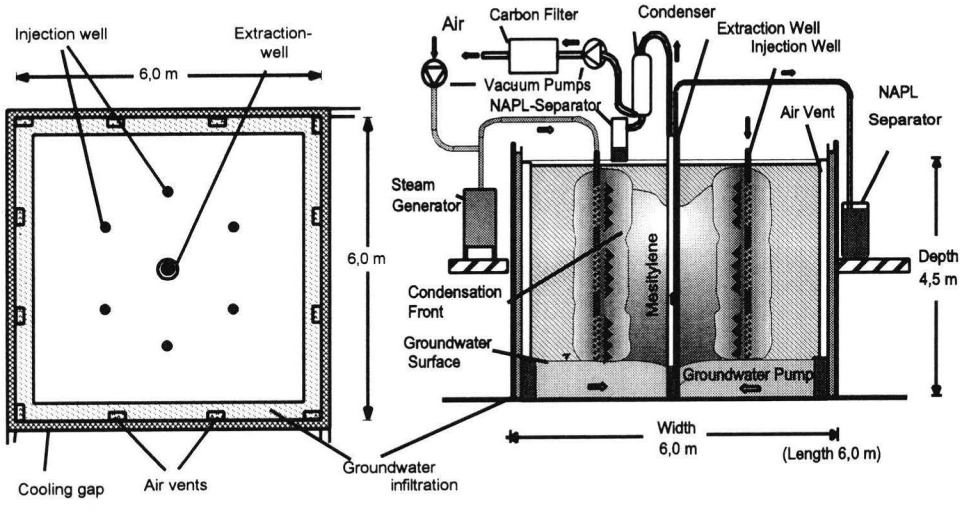
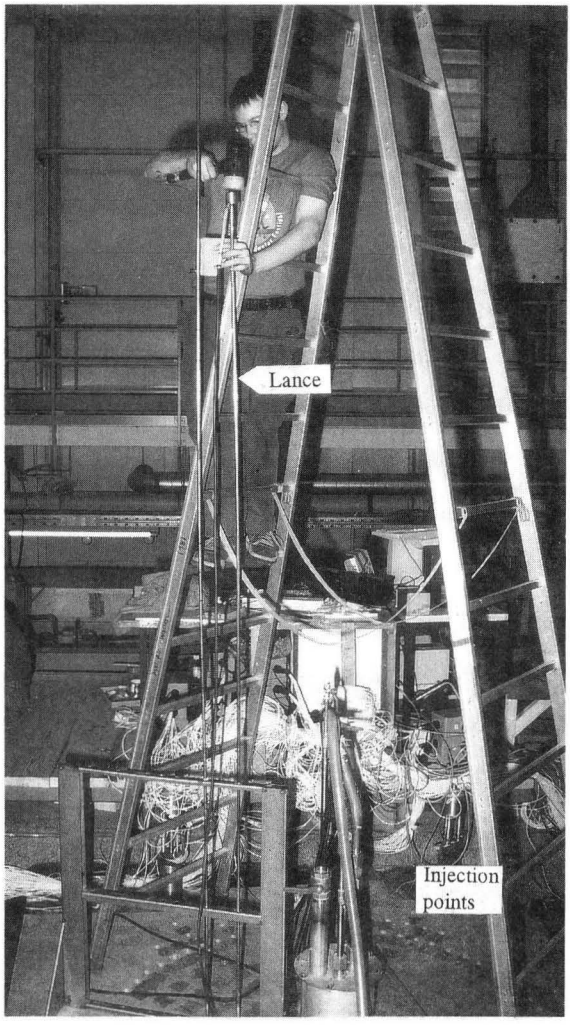


Fig. 3: Planview and cross-section of the experimental *VEGAS*-container setup.



During the experiment, groundwater, gases and liquid phase contaminant were removed from the central extraction well. Gases flowed through a 200 kW condenser and the condensate was passed into two separators; a 2-stage, 14 L glass separator and a 26 L steel separator, both with continuous flow. Noncondensible gases were passed through an activated carbon filter before being vented to the surrounding atmosphere. Air entered the sand from twelve vents located around the edge of the container. The groundwater was pumped from the bottom of the container and then passed through a two-stage 1200 L steel separator as a measure against contaminant loss. Liquid phase contaminant was skimmed from the water table using a large pipette and vacuum pump. Water removed with the liquid phase was separated using a 5 L, glass separating funnel. The heat front was monitored throughout the container by 220 temperature sensors.

Fig. 4: Injection of the contaminant through the lance.

The experimental setup and measuring system were designed so that only small modifications are required for application in the field.

INJECTION AND RECOVERY OF THE CONTAMINANT

The sand was originally at residual water saturation ($\approx 10\%$) before injection. The contaminant, mesitylene (C_9H_{12}, boiling pt. 165°C, density 0.865 kg/L) was injected into the container between the injection wells and the extraction well to minimize mobilization of the contaminant to points outside the clean-up area.

A 4 m stainless steel lance (Fig. 4) was used to inject contaminant accurately and evenly throughout the contamination area. A total of 66.75 kg of mesitylene was

injected using 5100 points with an average of 13 grams of contaminant per point. The injection points were spaced radially by 5°, horizontally by 10 cm, and vertically by 10 cm. In Fig. 4 the distribution of the injection points on the ground are visible. The resulting spill was controlled and accurate for the purposes of a mass balance.

During the experiment, the gas phase, liquid phase, and dissolved phase of the contaminant was removed from the center well (Fig. 5). The masses extracted in each phase were compared as percentages of the injected mass.

Mesitylene in gas phase was removed through vacuum extraction and passed through a condensor and subsequent condensate through a NAPL separator and non-condensible gas through an activated carbon filter. The mass extracted was monitored by removing condensed liquid phase from the separator and recording the adsorption on the filter.

Mesitylene in liquid phase was removed using a large pipette connected to a vacuum pump. The pipette was used to skim the water table surface for mesitylene floating on top. The liquid phase was then separated from the skimmed water in a separating funnel and the mass was recorded.

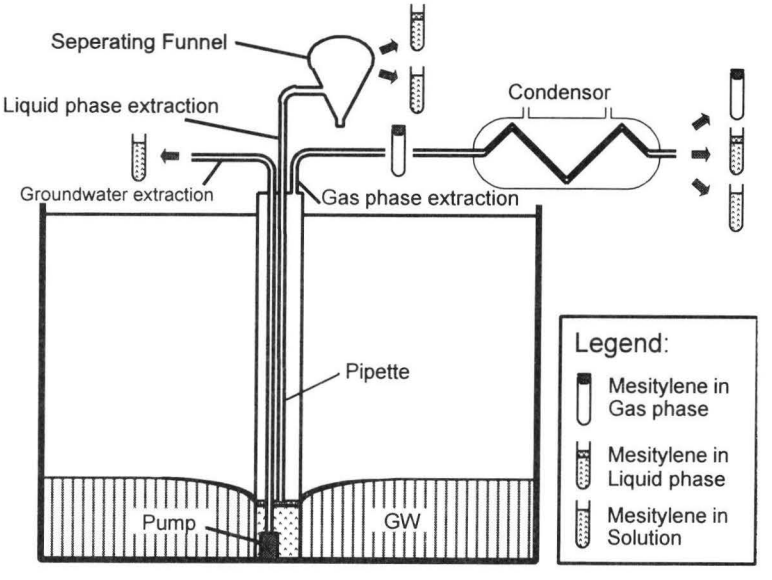


Fig. 5: The possible extraction points and phases of the contaminant.

Mesitylene in solution was monitored in all the water removed. Groundwater concentrations were sampled in the large separators. Condensate water was measured in the NAPL separator and water concentrations from the pipette were sampled from the separating funnel.

RESULTS AND DISCUSSION

The steam/air-mixture was initially injected into the container at a temperature of 60°C. As part of the sand was heated, the steam/air ratio was increased in order to increase the injection temperature (Fig. 2). The injection temperature was increased until the injection of pure steam was reached. The heat front created was wide with a moderate temperature gradient in contrast to the steep temperature gradient achieved with only pure steam injection (Betz *et al.*, 1997). The temperature distribution in the sand during steam/air injection can be seen in Fig. 6. The gradual heating of the soil is apparent as well as the stable movement of the front. The entire clean-up area was at elevated temperatures before pure steam injection began.

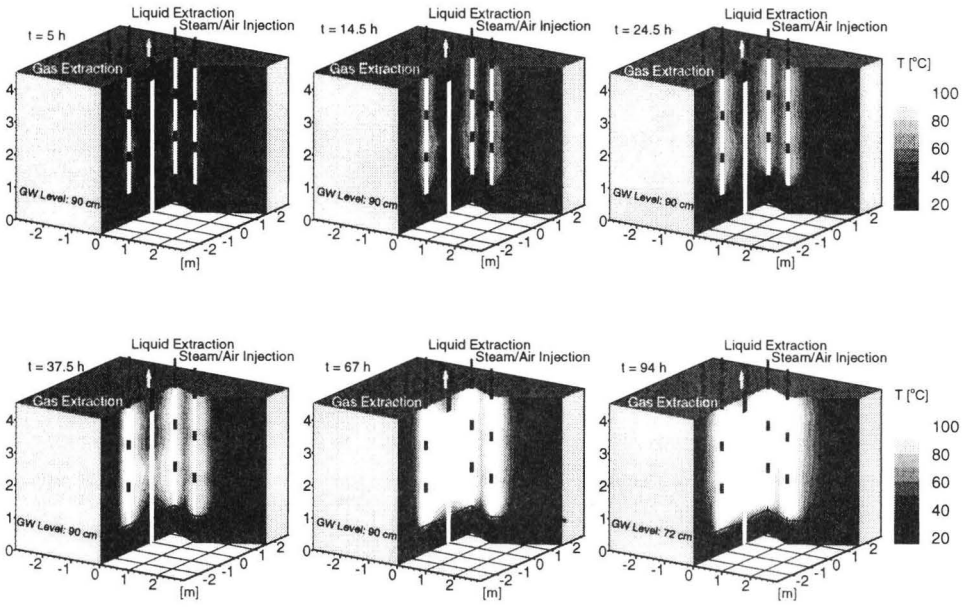


Fig. 6: Measured heat progression through the container during steam/air injection. The figure shows a cross-sectional temperature distribution after 5, 14.5, 24.5, 37.5, 67, and 94 hours in the experiment.

During pure steam injection, the sand was heated to 100°C within 20 h. Whereas, steam/air injection raised the temperature of the sand for several times longer in a gradual heating to pure steam temperatures (Fig. 7). Consequently during steam/air injection, the contaminant in the heat zone vaporized on a lower, more continuous rate than during pure steam injection. The total mass removal over time is shown in Fig. 8. A continuous contaminant flow was observed throughout the heating with a steam/air-mixture.

The earlier removal of contaminant observed with steam/air-mixtures compared to steam injection (Fig. 8) is primarily due to soil vapor extraction which was applied throughout the experiment. Initially vapor is removed at a rate determined by the vapor pressure of the contaminant. Typically with conventional SVE the mass removal will decrease exponentially over time. However, as the sand is heated more contaminant is volatilized and removed as a gas, maintaining the removal rate.

The removal rate observed during steam injection is steeper and breaks through after steam/air. The contaminant is vaporized in high mass levels and high mass transport in the gas phase occurs. The large masses of gas condense in the heat front and migrate to the water table. The contaminant moves en mass with the condensation front and therefore the main body of contaminant is removed as a liquid phase during steam breakthrough at the extraction well.

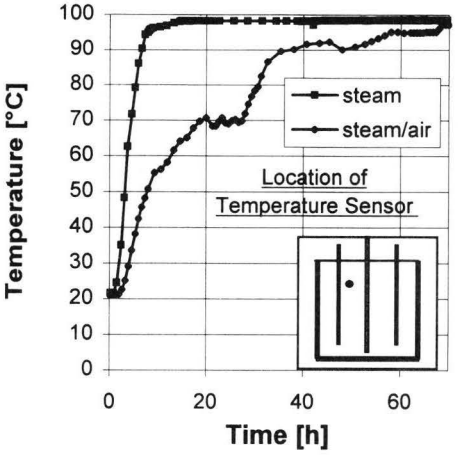


Fig. 7: Recorded temperatures at the same point during steam and steam/air experiments.

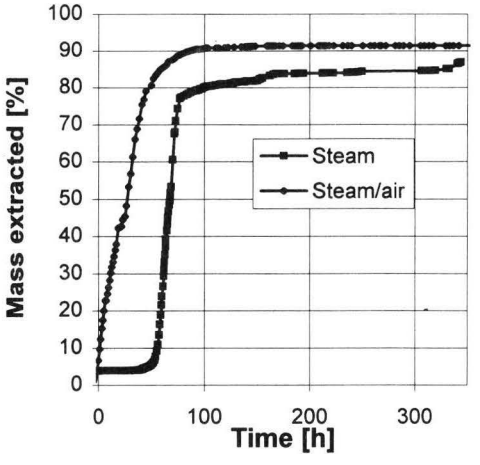
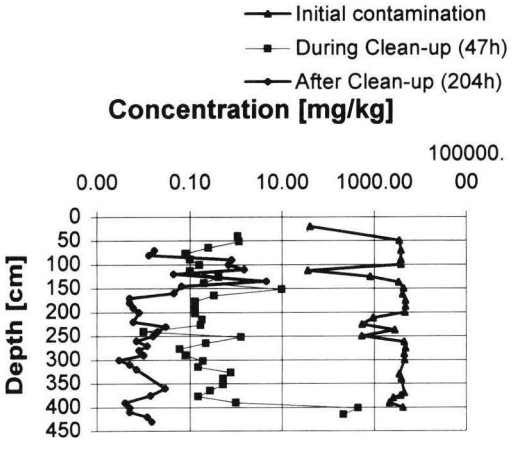


Fig. 8: Comparison of the mass removal rates of steam and steam/-air injection.

Table 1 illustrates the significant differences in mass removal, from liquid phase removal (steam) to gas phase removal (steam/air). This is noted in the high levels of contaminant removed through the condensor and the actived carbon filter during steam/air injection. With steam/air injection only 8.38% of the injected mass was removed by the pipette. Contaminant on the water surface during steam/air injection was due to cool temperatures in the extraction well interacting with a warm gas causing condensation in the well. Pure steam injection results in most of the contaminant mass being removed by skimming the water table surface where downward migration has caused it to pool. This is evident in the mass percentages removed by the pipette. Around 10% of contaminant during steam injection was removed as a gas after steam breakthrough. The concentrations of contaminant in the groundwater were also higher during pure steam injection.

Table 1: Comparison between the contaminant mass (as a percent of the total mass injected) removed by steam injection and steam/air injection.

	Steam	Steam/air
Pipette (Liquid Phase)	74.50	8.38
Condensate (Gas Phase)	4.46	27.99
Condensate (In Solution)	<0.001	0.34
Activated Carbon (Gas Phase)	5.42	54.42
Groundwater (In Solution)	2.44	0.65
Total Mass Removed (Percent of total mass injected)	86.82	91.78



This is further evidence that downward migration of the contaminant was significantly reduced during steam/air injection. Contaminant concentrations in the water are directly related to how much contaminant is in contact with the water. The concentrations in the condensate water were higher during steam/air injection due to more contaminant present in the NAPL separator. The steam/air injection was highly effective in removing a higher mass of contaminant as a gas.

Fig. 9: Soil sample concentrations from vertical cores taken in the clean-up area.

The total mass removed in the steam/air injection experiment was comparable within 5% to that of the steam injection experiment. Missing mass is attributed to the total analytical inaccuracy.

In order to determine the clean-up levels achieved, soil samples were taken from a vertical bore hole throughout the experiment. The samples were taken before, during (47h), and after (204h) steam/air injection (Fig. 9). Contaminant concentrations were reduced significantly over the duration of the experiment.

The relatively high concentrations seen near the bottom of the column in sample two are located in the capillary zone. Contaminant stays trapped in the capillary fringe (due

to low permeabilities) after the contaminant injection process. To eliminate these concentrations the pumping rates were increased to lower the groundwater table after the surrounding area was at steam temperature. Soil sample analysis showed concentrations of less than 1mg/kg after the experiment. Concentrations are much lower than the acceptable clean-up levels published in the Netherlands list (B-value for mesitylene: 7mg/kg).

CONCLUSIONS

In an effort to overcome the negative effects of steam injection such as, the downward migration of contaminant, a steam/air-mixture was injected into contaminanted soil beginning at lower temperatures than that of steam. Comparison of the steam/air injection experiment to a previous steam injection experiment revealed success in eliminating the downward mobilization of the contaminant to the water table. Contaminant was removed in the gas phase during steam/air injection instead of as a liquid phase with the condensation front, as seen in steam injection experiments. The mass removed was a higher percentage of the total mass injected than observed in a steam injection experiment. The soil samples after clean-up showed low concentrations ($<$ 1mg/kg) and therefore the remediation was very successful.

ACKNOWLEDGEMENTS

The financial support for the experimental studies of the *Projekt Wasser-Abfall-Boden (PWAB)* of the state-government of Baden-Württemberg, Germany is greatfully acknowledged. We wish to thank the anonymous services for their highly constructive suggestions.

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PERMEABLE TREATMENT WALLS FOR IN-SITU GROUNDWATER REMEDIATION - HOW TO AVOID PRECIPITATION AND BIO-CLOGGING

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Key words: in-situ groundwater remediation, reactive barriers, adsorption, degradation, construction design

SUMMARY

The design of permeable reactive barriers is discussed with reference preventing negative effects such as inflow of fine soil particles, precipitation of carbonates, iron and manganese, and loss of effectiveness by uncontrolled growth of biomass. A wall construction system including filter layers, permanent spacing for refillable reactive media and seals for stormwater- and air tightness is presented. Field test results are reported which show the system functions well and is effective at removing organic solvents from groundwater.

KURZFASSUNG

Für unterirdisch durchströmte Wände zur in-situ-Grundwasserreinigung werden Konstruktionsanforderungen dargestellt, mit denen das Zusetzen durch feine Bodenpartikel, die Ausfällung von Karbonaten und von Eisen und Mangan sowie der Verlust an hydraulischer Durchlässigkeit durch übermäßigen Bewuchs durch Mikroorganismen vermieden werden können. Ein entsprechendes Wandsystems mit Filterschichten, einem stabilen Innenraum zur Aufnahme der Reaktionsmaterialien sowie mit Abdichtungen gegen das Eindringen von Niederschlag und Oberflächenwasser wird vorgestellt. Ergebnisse von Feldversuchen belegen die Wirksamkeit der Entnahme von organischen Lösungsmitteln aus dem Grundwasser.

RÉSUMÉ

La conception des barrières réactives perméables est en cours de révision afin de prévenir des conséquences négatives telles que l'afflux de fines particules de sol, la précipitation de carbone, fer et manganèse, ainsi qu'une perte de la conductivité par une croissance incontrôlée de la biomasse. Un système de construction de murs comprenant des feuillets filtrants, un espace permanent supplémentaire pour les matériaux réactifs et des joints d'étanchéité prévenant l'infiltration d'eaux de surface et d'air, est présenté. Les résultats des tests de terrain montrent une bonne efficacité du système pour l'élimination des solvants organiques des eaux souterraines.

Contaminated Soil '98, Thomas Telford, London, 1998, 585–598

1. In-situ groundwater remediation with Permeable Reactive Barriers

According to EPA [1] "a permeable reactive barrier (PRB) is a passive in-situ treatment zone of reactive material that degrades or immobilises contaminants as groundwater flows through it. Natural gradients transport contaminants through strategically placed treatment media. The media degrade, sorb, precipitate, or remove dissolved organics, metals, radionuclides, and other pollutants. These barriers may contain reactants for degrading volatile organics, chelators for immobilising metals, nutrients and oxygen for microorganisms to enhance bioremediation, or other agents".

The following report is focused on construction methods that prevent negative effects which may reduce the effectiveness of the treatment media, negatively change the hydraulic conditions, or reduce the long-term PRB performance. This includes the application of knowledge and experience from groundwater well design and the evaluation of innovative technologies to remove and/or reactivate the treatment media in-situ.

Permeable Reactive Barriers have commonly been or are designed to be installed through excavation and replacement. This method is limited to approximately 8 m in depth, and the costs becomes prohibitive at greater depths. Alternative installation methods for greater depths include slurry wall construction, high pressure jetting, deep soil mixing, and hydro fracturing in the United States [2]. In Germany large diameter vertical borings, slurry methods and a modified deep wall construction are under evaluation or investigation, but have not yet been tested in the field.

2. Design objectives for Permeable Treatment Walls

The hydraulic behaviours of the two major permeable treatment wall design types - funnel and gate systems or continous reactive walls - are based on the hydraulic permeability of the whole construction system, including permeability of filter layers, screens and the treatment media itself. The system permeability of the wall construction should be at least two times higher than the permeability of the aquifer. It might be better to choose a factor of 10 times higher permeability for the wall system with respect to all limitating parameters that will reduce permeability with time. The major limitating factors are expected to be as follows:

- inflow and settling of fine-grained soil particles, which will block the pore spaces and reduce the permeability;
- precipitation of carbonates such as calcium or magnesium carbonates, iron oxides/hydroxides, and ferrous carbonate or other metal precipitants in the filter layer or the treatment media;
- uncontrolled growth of microorganism, such as bio-clogging;
- other, mainly long-term and unknown effects, which may reduce the permeability.

The following design objectives are focused mainly on the use of activated carbon as the treatment media. But most of this design objectives may also be useful if zero-valent iron (ZVI) or other media are choosen as reactive filling material.

Major design objectives are:

- Prevent the inflow of fine-grained soil particles by installing a filter layer between the adjacent soil and the treatment media according to the well-known filter criteria;

- Prevent changes to the physical and chemical properties of the groundwater such as
  - temperature,
  - pressure,
  - pH-value,
  - oxygen-content (Redox-potential),
  - nutrients,

  or be a ware that those changes will result in precipitation or microorganism activity which might be of advantage in specific cause;

- Design a wall-system which allows the removal and replacement of the treatment media after a period of several years or decades;

- Design a pipe-system in the wall to allow the injection of water and/or air for flushing to eliminate precipitants or sludges or to remix the media by turbulence;

- Design openings for inspection, removal or sampling of the treatment media.

WCI Umwelttechnik GmbH has patented a treatment wall construction system with regard to the above mentioned design objectives which can be installed in an open trench. The trench is excavated and stabilized prior to the installation of the wall construction.

3. Design of the Permeable Treatment Wall

WCI Umwelttechnik GmbH has developed a special method of wall construction which allows the adsorbing or other reactive media to be recovered without the need to demolish and rebuild the wall structure. The patented system includes filtration layers to prevent inflow of fine soil particles and measures to avoid precipitation by oxidation of iron and manganese.

As shown in Figure 1, the main design components are:

- a filter layer, consisting of gravel or sand pack, located between the trenched aquifer and the interior wall elements;

- interior wall elements, made of specially designed brick elements or precast concrete shells to define an interior filling space for the treatment media including openings for the groundwater through flow and horizontal elements to stabilise the earth pressure;

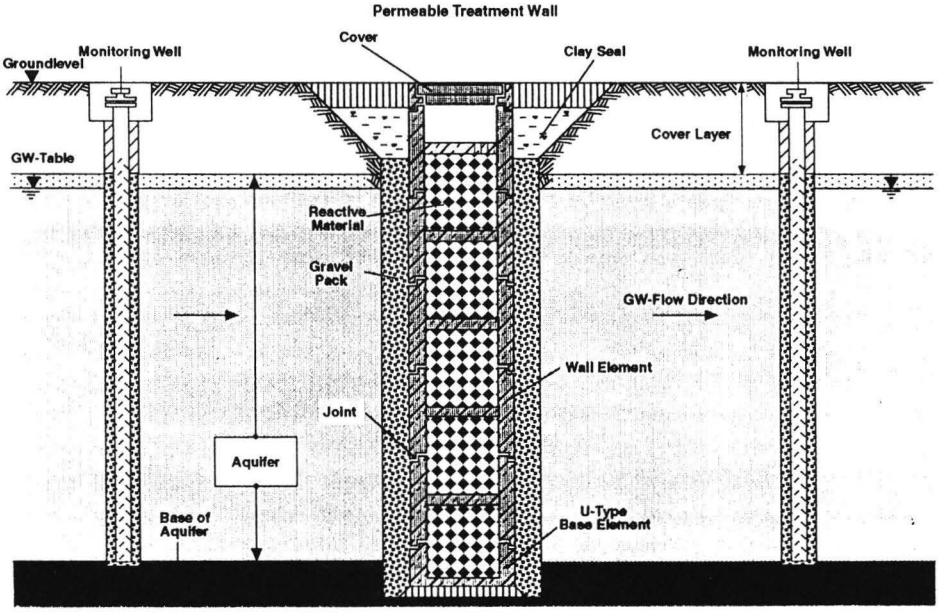


Fig 1: Permeable Treatment Wall Construction

- a clay seal to prevent inflow of stormwater and contact with atmospheric;

- a coverplate as an opening device for the recovery and replacement of the treatment media - additionally these covers can be made waterproof and airtight.

Some typical dimensions are shown for the cross section of the wall construction in figure 2.

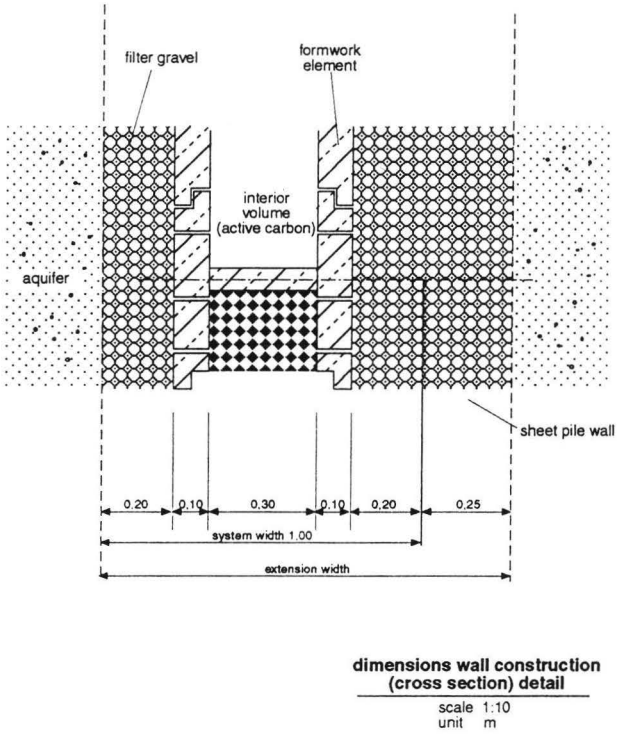


Fig. 2: Cross Section - Treatment Wall

Depending on the usually low groundwater flow velocity, the retention time of groundwater in a 0.30-m thick treatment media layer is between several hours and one or two days.

In order to dimension the retention time and media thickness new approaches must be developed based on test results in the field. In particular for the use of activated carbon, the retention time, surface capacity and the hight width (thickness) of media layers in the permeable treatment walls will differ widely from those dimensioning criteria used in conventional aboveground activated carbon filters (Table 1).

Table 1: Dimensioning criteria

Dimensioning Criteria	PRB-adsorbing	Conventional Activated Carbon Filter
Retention time	5 - 30 hrs	1 - 2 hrs
Surface load capacity	0.02 - 0.06 m/h	10 - 15 m/h
Height/width filter layer	0.3 - 0.5 m	2 m

4. Installation methods

The installation methods are described in detail in Figures 3 to 8.

In phase 1 (Fig. 3) sheet pile walls will be driven into the earth. The distance between the piles will be 1 m or more, according to the chosen system width. The sheet piles will be installed to 2 m into the bottom layer of the aquifer.

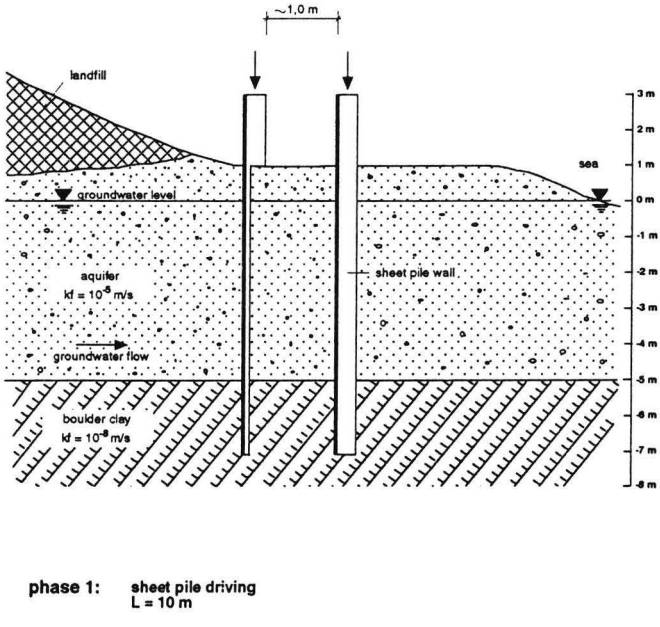
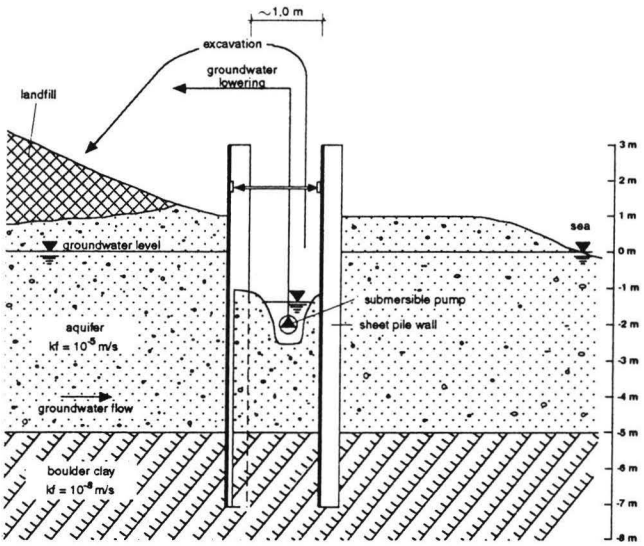


Fig. 3: Construction Phase 1

In phase 2 (Fig. 4) excavation will commence within the two sheet pile walls. An open ditch will be used to lower the groundwater table below the excavation level.



phase 2: **excavation and dewatering of the sheet wall construction**

Fig. 4: Construction Phase 2

After completion of the excavation (Fig. 5), a concrete base layer will be cast in situ and dewatering will be continued. The horizontal earth pressure will be supported with beams.

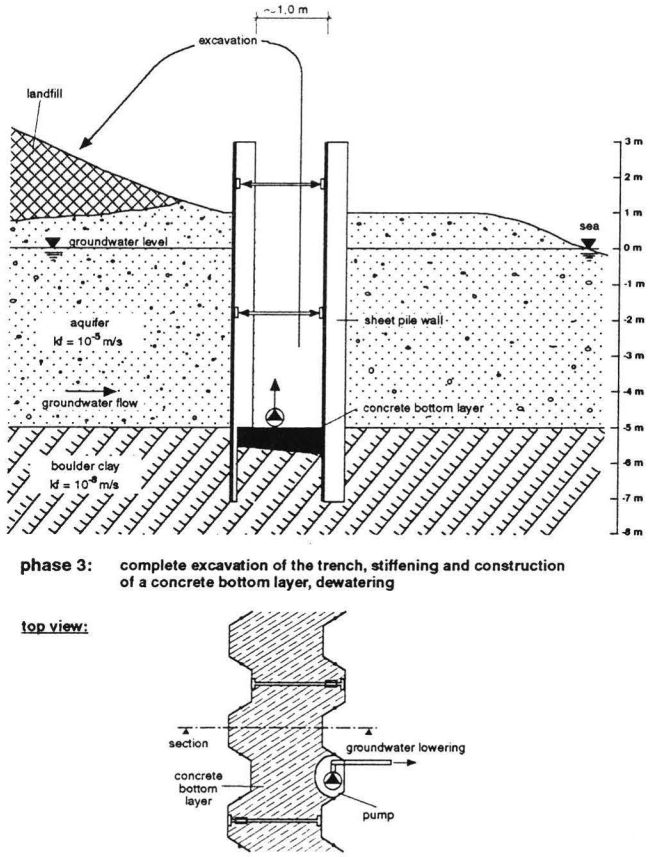
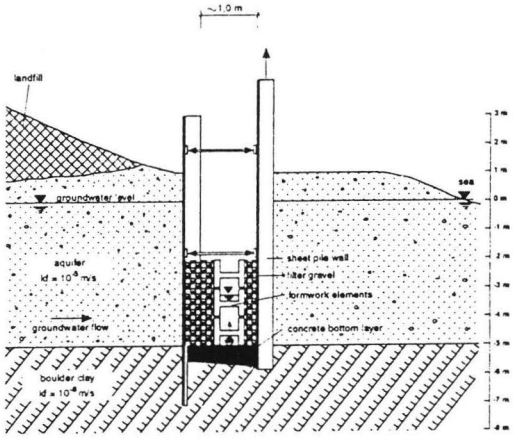


Fig. 5: Construction Phase 3

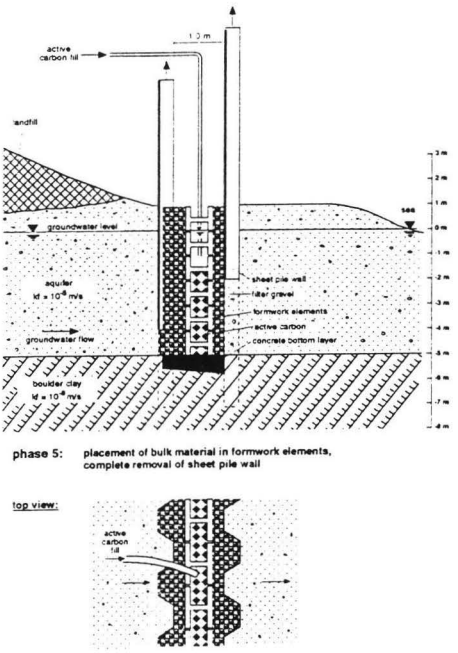
Now the installation of the formwork elements and placement of the filter gravel can begin on the concrete layer (Fig. 6). Its the construction grows, groundwater level can be allowed to rise again.



phase 4: placement of formwork elements, placement of gravel pack, partial removal of sheet pile wall, recovery of groundwater level

Fig. 6: Construction Phase 4

As the wall construction continues (Fig. 7), sheet piles can be raised accordingly and the treatment media will be filled into the interior space of the formwork elements.



phase 5: placement of bulk material in formwork elements, complete removal of sheet pile wall

Fig. 7: Construction Phase 5

Finally, the wall cover, the clay seal and some other measures can be installed to complete the construction (Fig. 8). Additionally bank protection (if located near a shore as in the give example), monitoring wells and a roadway for the tank trucks (to remove and replace the treatment media) may be installed.

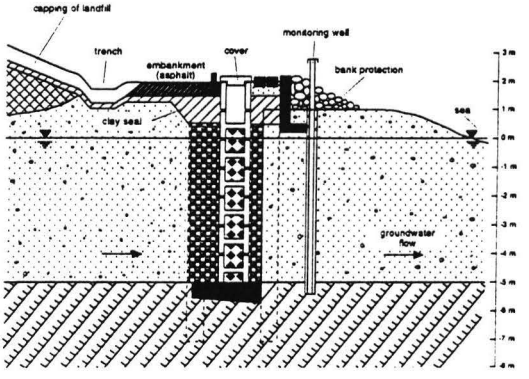


Fig. 8: Construction Phase 8

In Figure 9 a longitudinal section shows on approximately 30-m long constructed section. All the necessary installation phases from excavation to covering the complete wall are illustrated in such a section. For longer walls, several construction sections may be useful.

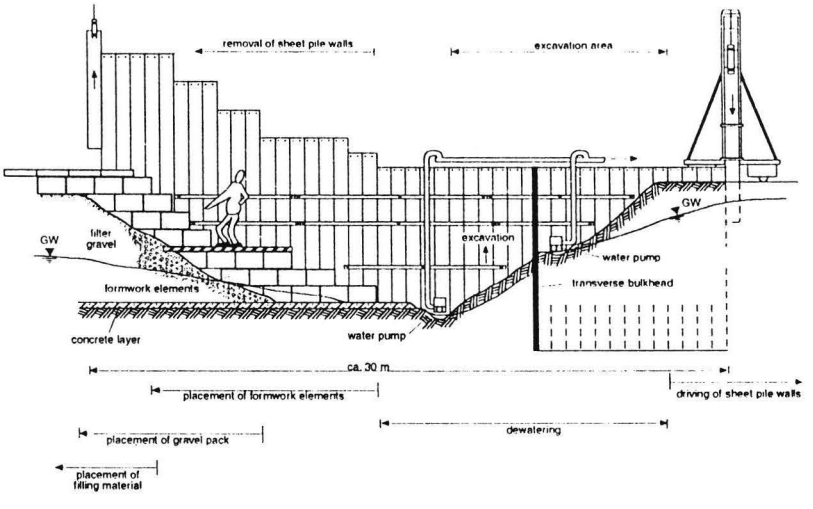


Fig. 9: Construction Progress in Logitudinal Direction

The construction costs for permeable treatment walls with a depth of 8 m are calculated to range from DM 850 to 1400,-- /m² (500 - 900 US-$/m²) without the treatment media (additional DM 300,-- /m² (US-$ 180/m²) for an activated carbon layer of 0,3 m thickness).

The width of the treatment media layer may vary with the length of the wall structure. In the middle of the contamination plume, where contamination is expected to be much higher, the dimensions of the reactive material should be in relation to the total freight of contaminants to be adsorbed (Fig. 10). A second wall structure, limited to areas of higher contaminant flow, may help to equalize the long-term performance along the longitudinal stretch of the wall structure.

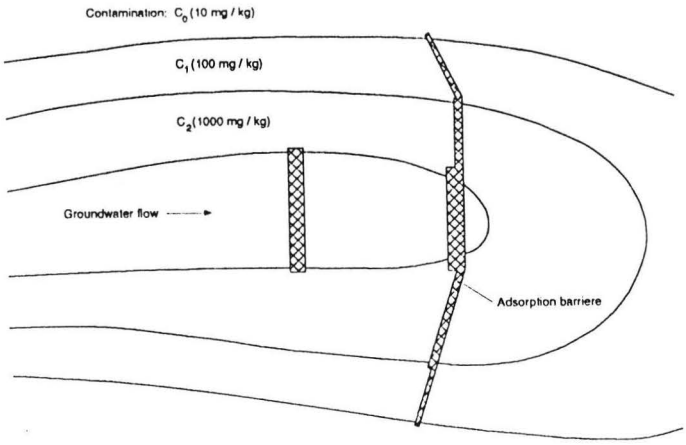


Fig. 10: Layout according to concentration levels

5. Precipitation

The potential for precipitation of calcium and magnesium carbonate mainly depends on the hardness of the groundwater, temperature, pressure and carbon-dioxide concentration. Usually the equilibrium of calcium and carbon dioxide within a given range of temperature and pressure will be heavily influenced by pumping the groundwater to an above-ground treatment system. The resultant effect is the precipitation of calcium carbonate on filters or inside stripping columns in the groundwater treatment plant.

One of the advantages of using permeable reactive barriers with a fill of activated carbon is, that neither temperature, pressure, or carbon-dioxide concentrations will be changed in the groundwater as it flows through the wall structure. Negative effects that cause precipitation of calcium carbonate may be avoided in this way. Covering the filter layers and the treatment media to match with the thickness and qualities of the existing

unsaturated zone will help to keep temperature, carbon-dioxide concentration and pressure in the given range.

In general, all changes to groundwater chemistry and physical conditions may result in negative effects. Intensive investigations and analysis of groundwater will help to evaluate the potential for precipitation or other limitating factors.

Precipitation of iron or manganese is also a well known effect for the design of pumping systems, wells and treatment plants. Often precipitation of iron or iron oxides is related to the increase of oxygen in groundwater. Well screens and stripping columns are blocked by iron precipitates due to the increased availability of oxygen.

Besides chemical reactions related to changes in pH and other parameters, the main focus in using activated carbon as a treatment media should be on how to prevent an increase of oxygen in the groundwater. Generally the top of the Permeable Reactive Barrier should be carefully sealed by clay layers or rubber seals to prevent inflow of oxygen with atmospheric air.

6. Bio-Clogging

Activated carbon is an ideal settling media for microorganisms. The adsorbed organics may be used as nutrients if desorbing effects can reactivate the concentrated contaminants. One of the major concerns related to microorganisms is that their biomass may block the reactive zones of adsorbing or other reactive media. Theoretically, the aerobic bioactivity can be controlled by reducing the delivery of oxygen and other nutrients.

As a result of the above mentioned effects, an uncontrolled growth of biomass can be limited by keeping the wall construction water- and airtight.

On the other hand, a controlled biomass may help to degrade contaminants directly on the carbon and help to prolonge the long-term performance of the adsorbant capacity.

Long-term field studies should be performed to evaluate the control of biomass on Permeable Reactive Barriers. At the present time we do not have enough experience to precisely calculate the influence of biomass activity on the effectiviteness of the treatment media.

7. Field Test Results

WCI conducted a field test for a period of five months in 1997 at a site in the Western part of Germany. The site is contaminated with many different chlorinated and nonchlorinated solvents. Benzene, ethylbenzene, toluene, xylene and trichloroethene have been detected in groundwater at high concentrations. Soil permeability and groundwater flow velocity are low. The aquifer itself is several meters thick. The maximum depth of a permeable treatment wall is 12 meters below ground level. A

continous wall segment with a length of 40 m is planned including two wings of vertical slurry wall barriers with lengths of 50 and 80 m.

With a 0.7-m thick filling of activated carbon the wall is designed to operate for at least 30 years before the first recovery and replacement of the media would be necessary.

The field test objectives were:

- to evaluate the choice of the best available activated carbon material within given economical limits;
- to test the period of performance until the first contaminant break through;
- to test treatment efficiency by analysing water quality and the inflow and outflow of the test equipment;
- to evaluate the effectiveness of the gravel filter;
- to evaluate precipitation of iron and manganese;
- to evaluate bio activity.

The test results are as follows:

- activated carbon commonly used in drinking water treatment was found to be the most suitable and was choosen for field testing;

- the period for breakthrough was approximately five times higher than calculated - a much thinner layer of reactive media is sufficient;

- no pressure losses through operation have been detected;

- treatment efficiency was as expected - all major organic contaminants were below the detection level;

- no precipitation was detected;

- biomass grew specifically in those areas of the carbon with high adsorbed organic mass, no visual biomass and no loss in hydraulic performance could be detected;

- the balance of inflow, accumulation and outflow concentrations was correctly identified in the analysis.

The field test equipment, including two columns of activated carbon to be operated under parallel condition, was proved to be usable for such tests. One column was tested under real time conditions, the other with a factor of 333 times faster. Regarding the faster column to differ from site conditions as residence time in the reactive zone in the second column is short due to the high-volume flow, the comparison of both columns gives good quality information for choosing design criteria for the full-scale implementation.

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IN-SITU REMEDIATION USING RADIO-FREQUENCY HEATING

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Key words: In-situ remediation, bioremediation, volatilization, immobilization, soil clean-up, organic contaminants, thermodesorption.

SUMMARY

Radio-frequency (RF) heating was applied for two different methods of soil clean-up : the thermodesorption of volatile contaminants and the enhancement of the microbiological remediation by moderate temperature increase. The thermal treatment up to a final temperature of 160°C was successfully applied to a real soil, which was contaminated with a light oil. All hydrocarbons up to naphthalene and n-tetradecane were removed with efficiencies > 99 %. The technique is able to achieve temperatures above 250°C. It could be proved that the RF radiation does not inhibit the biological activity in the soil. A specially designed matching network allows the introduction of radio-frequency electrical energy into soils with efficiencies > 90 %, even when they are completely dry or frozen.

KURZFASSUNG

Kontaminierter Boden wurde mit Hilfe von Radiofrequenz(RF)-Strahlung erwärmt. Dabei wurden zwei verschiedene Reinigungsmethoden getestet : die Thermodesorption von flüchtigen Schadstoffen und die thermisch unterstützte mikrobiologische Reinigung. Aus einem mit Leichtöl kontaminierten, realen Boden konnten durch Erhitzen bis auf 160°C alle Kohlenwasserstoffe bis Naphthalin und n-Tetradekan mit Ausbeuten > 99 % entfernt werden. Die Technologie gestattet Behandlungstemperaturen oberhalb von 250°C. Es konnte gezeigt werden, daß die RF-Strahlung die biologische Aktivität im Boden nicht inhibiert. Ein spezielles Anpaßgerät ermöglicht die Einbringung der RF-Energie mit Wirkungsgraden von über 90 % in Böden auch dann, wenn diese ausgetrocknet oder gefroren sind.

RÉSUMÉ

Le réchauffement par ondes a été appliqué pour la décontamination de sols par le biais de deux méthodes différentes : la thermodésorption de polluants volatils et le développement de l'assainissement micro-biologique à température modérée. Le traitement thermique a été réalisé avec succès sur un sol réel, contaminé par des hydrocarbures légers, jusqu'à une température finale de 160°C. Tous les hydrocarbures, y compris le naphtalène et le n-tetradécane ont été extraits avec des rendements supérieurs à 99 %. Le matériel permet d'atteindre des températures au-delà de 250°C. Il peut être prouvé que les ondes radio n'inhibent pas l'activité biologique. Le degré de dégradation du phénol est identique pour des échantillons chauffés grâce aux ondes radio ou grâce à un bain d'eau traditionnel. Un circuit électrique spécialement élaboré permet l'introduction d'énergie électrique de haute-fréquence dans le sol avec un rendement supérieur à 90 %, même si le sol est totalement sec ou gelé.

Contaminated Soil '98, Thomas Telford, London, 1998, 599–607

Radio-frequency (RF) heating method

The wide variety of subsurface contamination characteristics (soil to be treated, spectrum and profile of contaminants, specific site conditions) requires the development of new remediation techniques. Ideally, they should be applicable on-site in order to minimize remediation costs.

Soil heating by radio-frequency (RF) treatment attracts increasing interest as a unique in-situ method which allows controlled and relatively high heating rates throughout significant volumes[1-3]. The method can be applied to heat electrically non-conducting dielectric materials and its working principle can be compared with a microwave oven. However, due to the lower frequency of RF waves (3 to 50 MHz), much larger volumes can be treated. Microscopically, the heat is introduced by rapidly changing the orientation of intrinsic dipoles resulting in the so-called dielectric loss. In the remediation application, the soil represents the dielectric of a capacitor, and the plates of the capacitor are often substituted by rod-like electrodes inserted into boreholes. In contrast to other heating methods which rely on heat conduction and fluid convection within the soil, RF heating results in an immediate temperature increase throughout the whole volume. This may lead to faster, energetically effective site processing combined with the advantage of minimal environmental impact as is typical for RF treatment. The heating method can be combined with various remediation techniques, especially soil vapour extraction (thermal desorption), stripping and biodegradation[1,2] with the aim of enhancing the efficiency of degradation.

In the present study, RF heating was exemplarily applied for two purposes of fundamental importance for the application of this method: (i) to stabilize an optimum temperature for biological remediation and (ii) to enhance the desorption rate of contaminants from soil by increasing their vapour pressure and diffusivity. Laboratory and pilot plant investigations have been carried out to study the range of available temperatures, the entire energetic efficiency, the dependance of the heating profile on the arrangement of the electrodes and a possible influence of the electromagnetic field on microbial activity.

Two RF generators (Hüttinger, Freiburg/Germany; operating frequency 13.56 MHz) having a maximal power of 1 and 5 kW were used for the experiments, the choice depending on the size of the soil-filled reactor. The RF generator was connected to the electrodes via a modified matching network (so-called matchbox, provided by Arbes, Berlin/Germany) in order to realize an optimal energy transfer to the soil. This equipment allowed a heating efficiency of more than 90 % of the RF power output. The soil temperature was continually measured by a fibre optics system (Nortech, Quebec/Canada). The heating rate and the parameters of the matching network were controlled by a computer system. A typical RF heating system which can be used either for facilitating thermodesorption or for stimulating microbial degradation is schematically represented in fig. 1.

In agreement with results from the literature[1-3] it could be demonstrated that the RF method allows the heating of soils in a wide temperature range from -20°C to about 250°C. In principle, even higher temperatures can be achieved since RF heating does not require the presence of water in the soil. However, when dry and wet regions simultaneously exist, the

heating rate of moist soil is significantly higher than that of the dry material. This effect results in a stabilization of the temperature around 100°C due to the evaporation of water initially present in the soil. A typical example, the RF heating of frozen soil containing about 16 wt.-% water to a final temperature of 100°C, is shown in fig. 2.

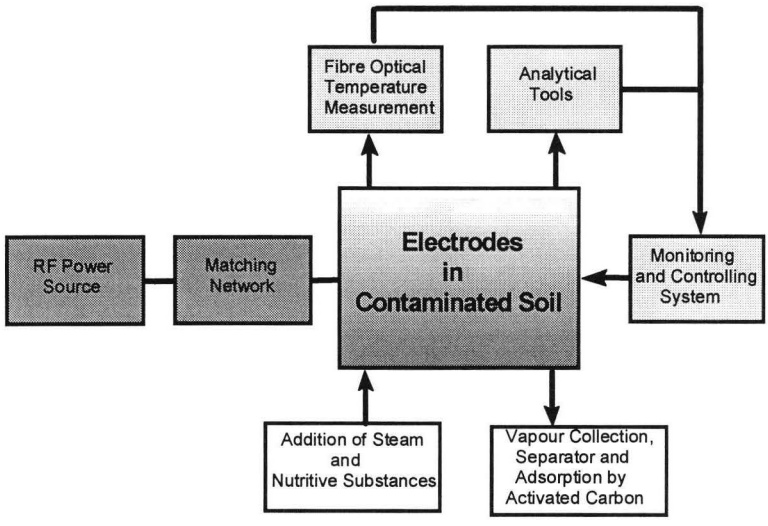

Figure 1 Scheme of an RF heating system which can be applied to support various remediation techniques

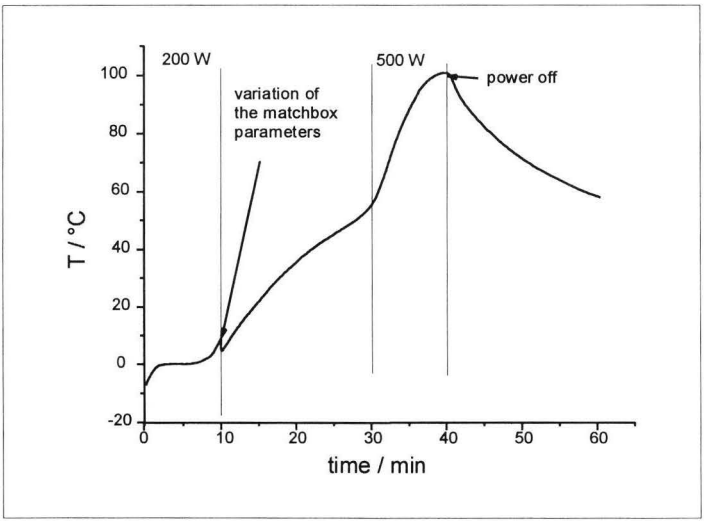

Figure 2 RF heating of an initially frozen soil sample (native humidity 16 wt.-%)

Application for microbial degradation

The RF heating technique can only be applied to microbial remediation provided that the biological activity is not inhibited by the RF radiation. Therefore, the effect of RF radiation was exemplarily studied with a phenol-degrading bacterium *Pseudomonas fluorescens* SV35. The strain was isolated from flocculated carbonization wastewater (Lake Schwelvollert, Saxony-Anhalt/Germany). *Pseudomonas fluorescens* was cultivated in a mineral salt solution[4,5] with 100 ppm phenol as sole carbon source at a temperature of 30°C. To test the degradation kinetics, a number of 1ml-aliquots of the pre-cultivated batch culture were distributed into 2ml-Eppendorf tubes. These tubes were placed either in a water bath or in a bed of dry sand in the RF reactor. In both cases, the temperature was kept constant at 31°C with an accuracy of ± 0.3 K. The phenol concentration as a function of degradation time was measured for two parallel samples colourimetrically[5] and by HPLC (Beckman); the two sets of results were in good agreement. It was found in all experiments that the degradation was not hindered by the electromagnetic field. This result was obtained for continuous (with an RF power of 6 W, HPLC quantification shown in fig. 3) as well as for pulse heating (applying 200 W pulses with 30 s duration at 15 min intervals, HPLC results represented in fig. 4). Therefore, this method can be successfully applied to enhance bioremediation techniques. The question whether the slight enhancement of the degradation rate of RF-heated samples in comparison to the samples situated in the water bath is a genuine effect has to be finally clarified by further experiments.

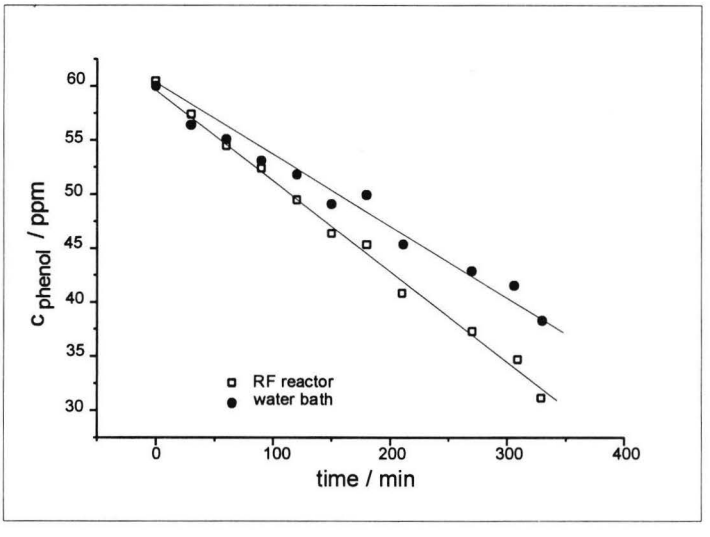

Figure 3 Phenol degradation by *Pseudomonas fluorescens* SV 35 at 31°C with the temperature stabilized either by RF application (continuous RF power 7 W) or by a water bath

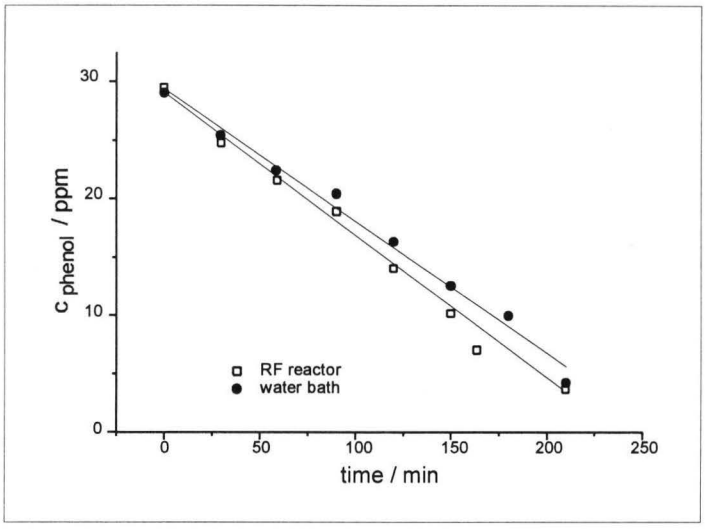

Figure 4 Phenol degradation by *Pseudomonas fluorescens* SV 35 at 31°C with the temperature stabilized either by RF application (200 W pulses of 15 s duration every 15 min) or by a water bath

Beside the investigations with a single strain, another method was applied to check the influence of the RF radiation on the biological activity as a whole. A large number of microorganisms present in the soil are able to reduce dimethylsulfoxide (DMSO) to dimethylsulfide (DMS) according to :

$$(CH_3)_2SO + 2\,e^- + 2\,H^+ \rightarrow (CH_3)_2S + H_2O\,. \qquad (1)$$

It is known that different enzymes in various cells catalyze this transformation. Therefore, it can be used as a measure of biological activity of a distinct population or microbial community. The corresponding method has been developed by Alef and Kleiner[6]. In the present study, an aerobically enriched culture was cultivated in a mineral salt solution[4,5] with 100 ppm phenol as sole carbon source at a temperature of 30°C. The microbial activity was quantified by the DMS formation rate for identical samples kept at 30°C either by RF heating or by a water bath. The DMS concentration was determined by headspace gas chromatography (DANI headspace sampler HSS 85.50 combined with a DANI 86.10 gas chromatograph). Again, no inhibition due to the RF heating was observed. This result was obtained for soil samples as well as for liquid cultures. As an example, the degradation of phenol and the simultaneous formation of DMS for the two differently heated samples are depicted in fig. 5.

The two different techniques were used to characterize the influence of RF energy application (i) on the degradation of a single substance (phenol) by a distinct strain and (ii)

on the DMSO reduction as a measure of the microbial activity. In both cases, the reaction rates were not diminished by RF heating. Therefore, RF heating can be expected to become a valuable tool for the optimization of biological in-situ and ex-situ remediation.

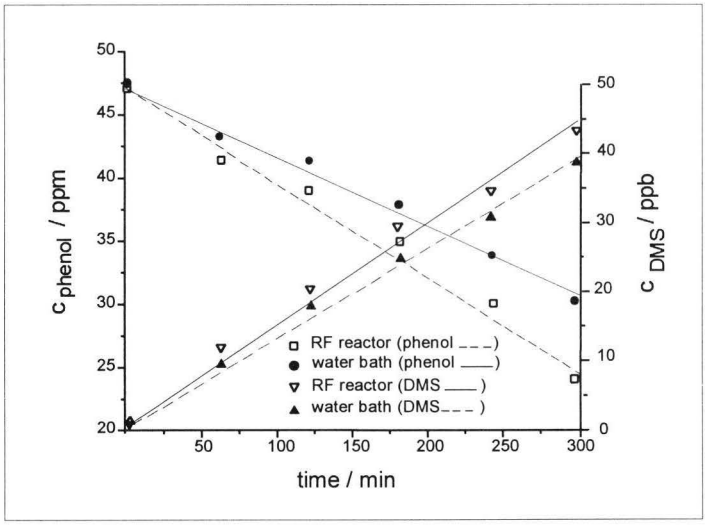

Figure 5 Phenol degradation and DMS formation compared for two samples of *Pseudomonas fluorescens* SV 35 kept at 30°C either by RF application (continuous RF power 7 W) or by a water bath

Application for thermodesorption

In addition to the microbiological application, RF heating is also applicable to enhance the desorption of organic pollutants from soil. This procedure can best be described as a thermally enhanced soil vapour extraction (TESVE) or as an in-situ thermodesorption. Two parameters in particular have to be optimized in order to achieve the highest performance : humidity and final temperature. In contrast to desorption from mineral surfaces, the influence of humidity on the desorption of organic compounds from soil organic matter (SOM) is not yet fully understood[7-13]. Therefore, one aim of the present study was to investigate the effect of water on the removal of volatile hydrocarbons from SOM.

As an example, the desorption of toluene from a humic acid (HA, from Roth Ltd.) is shown in fig. 6. First, the HA was equilibrated with toluene vapour for 24 h, in order to reach an equilibrium loading of about 10 000 ppm. The toluene-contaminated HA was then stripped in a flow of dry air (residual relative humidity rH below 1 %) leading to the desorption of weakly bound toluene (ca. 5000 ppm).

Subsequently, the stripped sample was divided into two equal portions, which were treated with two different procedures to initiate further toluene desorption : (i) Heating to 120°C in dry air led to a relatively narrow desorption peak and a final concentration of approx. 2500

ppm after 24 h. (ii) The second portion of the contaminated HA sample was exposed to wet air (rH approx. 90 %) at 30°C. This treatment resulted in a continuous desorption over more than 10 h and a final concentration of less than 100 ppm. Obviously, water has the ability to markedly increase the mobility of the organic pollutants in the humic acid by swelling or widening the organic matrix.

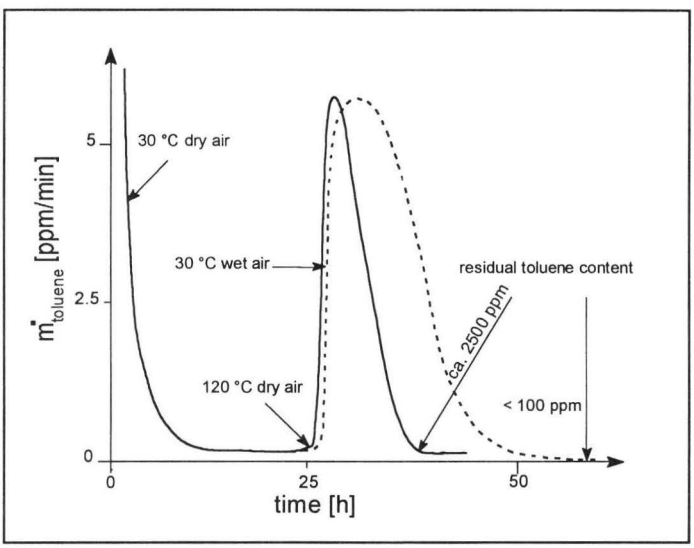

Figure 6 Desorption of toluene from humic acid into the gas phase using two different procedures (introduction of humid gas and thermodesorption)

This result, which was also found for other volatile organic substances, has important consequences for the optimization of the desorption process. Under a wide variety of conditions, the introduction of a certain humidity can be more effective than extra heating. Since RF heating can be applied over a broad range of humidity, the remediation costs can be minimized by the interactive influence of both parameters : humidity and temperature. In the case of toluene, the mobility of the sorbate is apparently the limiting factor for the overall desorption rate. For higher boiling compounds, such as SVOCs, the evaporation may be the slowest step. In this case, an optimized combination of humidifying and heating may be the most effective procedure.

From many experimental studies it is known that spiked samples and aged real soils behave significantly differently. Therefore, we applied the RF heating to a sandy soil from a former lignite pyrolysis factory, heavily contaminated with aromatics (BTEX and naphthalenes) and alkanes (C_{10}-C_{14}). 4 kg of the soil containing 11 wt.-% of native moisture and about 1000 ppm of volatile hydrocarbons were placed in the fixed bed RF-heater and purged with an air flow of 100 ml/min. Selected results are depicted in fig. 7. Naphthalene (c_0 = 8.2 ppm) is used here as a representative component of the hydrocarbon mixture.

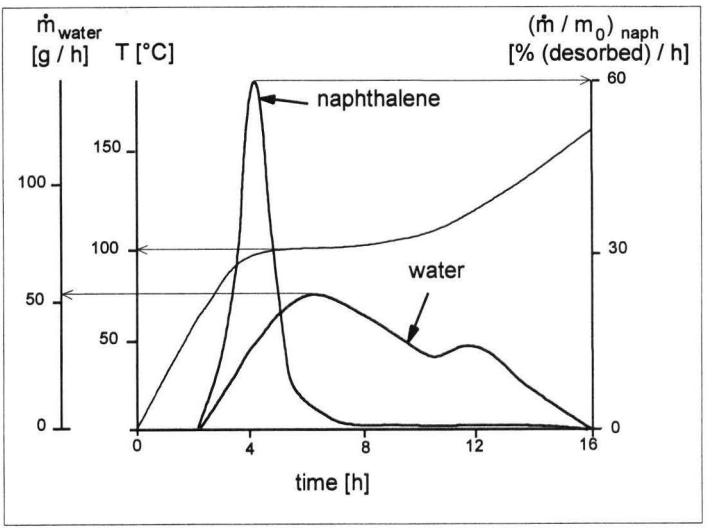

Figure 7 Desorption of naphthalene and water from a real soil as a function of temperature achieved by RF heating

The hydrocarbons desorbed simultaneously with the water (50 ml/h), starting at about 80°C. After 6 h purging at 100°C, more than 90 % of the contaminants were removed. The temperature was raised then to 160°C and held for a further 6 h. The soil was extracted (CH_2Cl_2) before and after the thermodesorption treatment and the extracts were analyzed by GC/MS. All the hydrocarbons were found to be depleted below the detection limit of 50 ppb per component. This corresponds to a removal rate of > 99.5 % for the main components. It is remarkable that some hydrocarbons which were present only in minor amounts (e.g. toluene, c_0 = 1.1 ppm) showed a desorption profile significantly different from that of the main components, typically flatter, indicating a slow diffusion step in the overall desorption process.

As shown by the laboratory and pilot scale investigations, RF heating is a variable and promising method to support remediation techniques such as thermodesorption and biological contaminant degradation.

Acknowledgement

The authors thank the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie (FKZ 1471052 and 1470975) for financial support and Mrs. B. Dommsch for technical assistance.

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HOW CAN AGRICULTURAL PRACTICES IMPROVE PHYTOREMEDIATION OF SOILS CONTAMINATED BY HEAVY METALS?

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Key words: bioremediation, contaminated soil, heavy metals, cadmium, zinc, plants, soil-to-plant transfer, fertilization, nitrogen, risk management

SUMMARY

A consequence of human activities is that trace elements released from anthropogenic sources have entered the environment and may alter the functioning of ecosystems and threat human health. On the other hand, research is revealing that hyperaccumulators of metals are a specialised class of plants able to take up and tolerate very large amounts of heavy metals in their shoots. Growth of hyperaccumulating plants on polluted soils, *i.e.* phytoremediation, seems to be a useful biological tool for remediating metal contaminated sites. This study was undertaken to determine whether the efficiency of phytoextraction could be enhanced through agronomic practices like fertilization. Trials were performed in pot experiments on an industrial soil and on an agricultural soil artificially polluted with Cd/Zn. A field experiment on agricultural soil was conducted to assess the impact on hyperaccumulation of different N fertility rates due to added urban sludge. Shoot dry matter production and leaf tissue heavy metal content of the hyperaccumulator *Thlaspi caerulescens* were determined. The evolution of total metal content and the mobility of remaining metals were followed with chemical extractions. Results were obtained in basic knowledge on the agronomy of hyperaccumulators and especially the role of N and P fertilization on metal availability and uptake. On a practical point of view, nutritional conditions confering the most favorable conditions for metal uptake were determined. Phytoremediation reduced the risk, extracting a high amount of the mobile metal in the soil. The methods used in the investigation may easily be adapted to a large number of hyperaccumulating plants and contaminated sites. The results provide substantial help in adapting phytoremediation at different soil fertility conditions. They lead to conclusions about the possible success and improvment of this treatment and the estimation of time required to obtain a satisfactory metal concentration in soil.

Contaminated Soil '98, Thomas Telford, London, 1998, 609–617

INTRODUCTION

The uncontrolled release of mineral chemicals as a result of human activities has changed in character and scale, due to intensification of industrial, agricultural and domestic activities. The source of pollution may be local, such as waste dumps, industrial landfills, or storage of dangerous substances. In many cases, chemicals are spread on the soil or are deposited from the atmosphere, leading to a widespread pollution throughout the landscape. Research work is revealing and demonstrating the evidence of heavy metal hyperaccumulation by some plants and growth of hyperaccumulator plants is seen as a biological alternative to physical and chemical treatments of soils contaminated with heavy metals (Baker *et al.*, 1993 ; Baker *et al.* 1994a, b ; Cunningham *et al.*, 1995 ; Morel *et al.*, 1997 ; Schwartz, 1997). However, the initial scientific efforts in the area of phytoextraction focused on the selection of the best metal extracting plants and not on the optimization of their laboratory and field performance by agronomical practices. Low nutrients rather than metal toxicities can cause low plant cover. Is then phosphorus (P) or nitrogen (N) the key element in NPK fertilization of the hyperaccumulating plant *T. caerulescens*? Up to what P or N fertilization rate the plant is growing : is the biomass production high enough to allow a significant metal uptake? Smith & Bradshaw (1979) showed that growth of the tolerant races of *Agrostis capillaris* L. on highly metal toxic mine spoils was greatly increased by P fertilization. Stress tolerant plants are hypothesised to have evolved adaptation mechanisms including low growth rates, and it is of particular interest to see how stress tolerators would respond to a pulse of P or N fertilization (Grime, 1979). The objective of this research was to evaluate the effect of P and N fertilization on plant growth and heavy metal uptake of *T. caerulescens*. Using pot experiments conducted in a glasshouse under controlled conditions and a field experiment, biomass production and heavy metal transfer to above ground parts of two different populations of *T. caerulescens* and *B. napus* were measured under increasing P and N (nitrate or ammonium) fertilization rates.

MATERIAL AND METHODS

Soil and plant material

Soil samples were collected from the Ap horizon of an agricultural soil located in Vannecourt (Moselle, France) and in the upper horizon of a soil in the vicinity of a former zinc smelter. Soil samples were air-dried and sieved through a 5 mm-mesh size before use in the experiments. Agricultural soil was a slightly leached brown soil (calcic cambisol : FAO classification) and was not contaminated by heavy metals and has a lowlevel of extractable P (Table 1).

Table 1. Heavy metals in the agricultural soil artificially polluted with Cd/Zn and in the agricultural soil from the vicinity of the former Zn smelter

	metal	HF extraction	NH_4NO_3 extraction	H_2O extraction
			mg kg^{-1}	
agricultural soil	Cd	5.1	1.6	0.2
+ Cd/Zn	Zn	490	192	30
agricultural soil	Cd	14.3	3.8	0.1
vicinity of Zn smelter	Zn	1 609	415	10

The hyperaccumulator *Thlaspi caerulescens* belonging to the *Brassicaceae* family was used in this study. Concentrations of Zn as high as 27,300 mg kg^{-1} have been reported in

the foliar dry matter of *T. caerulescens*. Seeds of *T. caerulescens* J. & C. Presl were obtained from a former Zn/Cd smelter site located in Prayon, Belgium (Vázquez *et al.*, 1992) and kindly supplied by A.J.M. Baker. Another population of *T. caerulescens* was collected on a former Zn/Cd smelter in Viviez (France). Seeds were stored at 4°C before use. *B. napus* was used as a reference crop.

Pot and field experiments

Phosphorus fertilization

Agricultural soil was amended with $Cd(NO_3)_2$ at a rate of 5 mg Cd kg^{-1}, $ZnSO_4$ at a rate of 450 mg Zn kg^{-1}, and with increasing rates of P as KH_2PO_4 (0, 0.1, 1, 10 and 100 mg P kg^{-1}). One kg soil of each treatment was added to plastic pots, and four pre-germinated seedlings of *T. caerulescens* were transplanted. Adequate uniform N-K fertilization was made. Pots were placed in a greenhouse. Controls without plants were prepared and conducted in the same conditions.

Nitrogen fertilization

Two other experiments were conducted on an agricultural soil amended with $Cd(NO_3)_2$ at a rate of 5 mg Cd kg^{-1}, $ZnSO_4$ at a rate of 450 mg Zn kg^{-1} and on an agricultural soil from the vicinity of a former zinc smelter (Table 1). Both soils were amended with increasing rates of N-nitrate or N-ammonium (0, 20, 80, 200 mg N kg^{-1}). No P fertilization was made.

Field experiment

For the last two years, we undertook a field experiment that focused on Zn and Cd extraction by *T. caerulescens* grown on an agricultural soil amended with heavy metal rich urban sludge (24 mg Cd kg^{-1} DM and 2 347 mg Zn kg^{-1} DM). Plots of 2 m^2 were amended with increasing rates of urban sludge (0, 3, 15 t ha^{-1} $year^{-1}$) and cultivated with *B. napus*, *T. caerulescens* Prayon and *T. caerulescens* Viviez. Plants were harvested, washed and dried. The shoot dry biomass was measured individually for all plants and they were divided in three different dry weight groups (C1 : $\leq$ 1 g ; C2 : > 1 g and < 5 g ; C3 : $\geq$ 5 g DM $plant^{-1}$). Shoot dry matter production and leaf tissue heavy metal content of *T. caerulescens* and *B. napus* were determined.

Analysis of metals in plant and soil samples

Plants were oven-dried 80°C during 48h. Ground dry plant material was mineralised with 2 mL H_2SO_4, 6 mL HNO_3 and 2 mL H_2O_2. The filtered extract was adjusted to 25 mL with 0,1M HNO_3 and was then analysed for total Cd and Zn by plasma emission spectrometry (ICP Jobin Yvon JY 38). Average values for five replicate determinations per treatment were computed.

RESULTS AND DISCUSSION

Production of plant biomass

Plants growing at different levels of P presented different dry matter productions and growth of *T. caerulescens* was significantly higher on metal-amended soils than on

controls (Figure 1). No symptom of metal phytotoxicity was recorded with *T. caerulescens* but *B. napus* exhibited visible signs of metal toxicity. *B. napus* produced higher biomass with additions of 10 and 100 mg P kg^{-1} than with lower rates (no presented results).

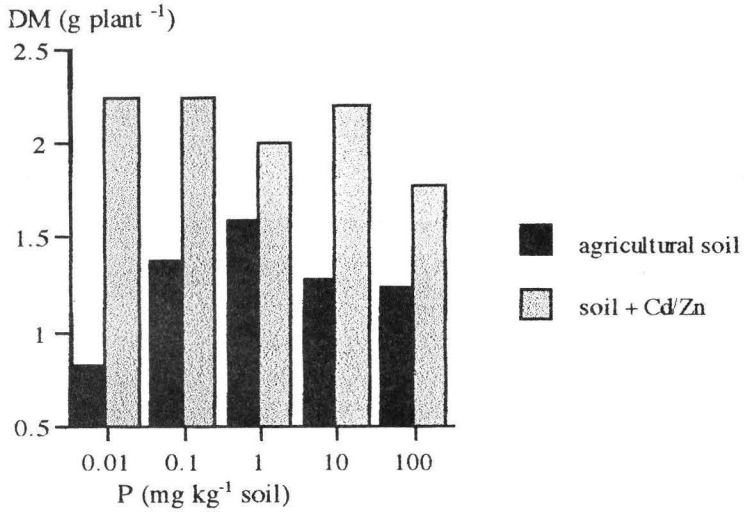

Figure 1. Dry weight yield of *T. caerulescens* grown at five levels of P fertilization

Nitrogen fertilization increased plant biomass and extraction of metals (Figures 2, 3 & 4).

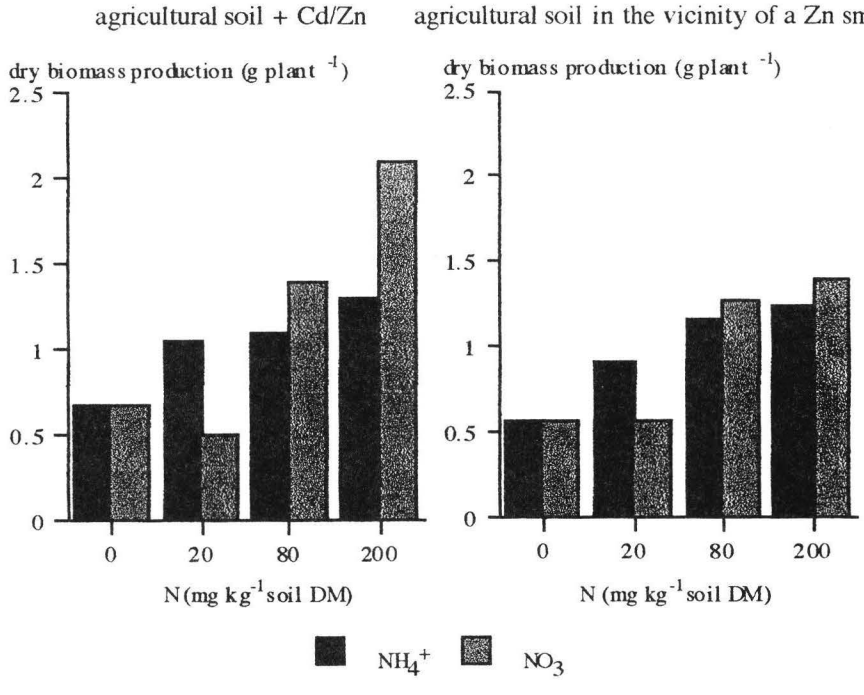

Figure 2. Dry weight yield of *T. caerulescens* grown at four levels and two forms of N fertilization

The optimum nitrogen rates for the contaminated agricultural soil and the agricultural soil from the vicinity of the Zn smelter were respectively 200 mg N kg^{-1} and 80 mg N kg^{-1}. On the two soils and like for other plant species, N-nitrate fertilization had an higher effect on the biomass production than N-ammonium.

Metal uptake

In the P fertilization experiment, uptake of Zn and Cd by *T. caerulescens* was significantly higher when no P was added to the soil. Concentration of metals in *T. caerulescens* varied from 4,100 to 6,900 mg Zn kg^{-1}, and from 40 to 63 mg Cd kg^{-1}.

In the N fertilization experiment, uptake of Zn and Cd *T. caerulescens* was strongly dependent on the N rates with marked differences between the two populations of *Thlaspi*. Metal content in *Thlaspi*-Prayon reduced significantly when N was added to the soil. This was probably related to a dilution effect due to the increased biomass production. Zinc concentrations in the leaves were higher with N-nitrate than with N-ammonium fertilisation. For *Thlaspi*-Viviez, the Zn concentration increased only with N-nitrate fertilization. On the contrary, the Cd concentrations were increased especially with N-nitrate fertilization. Cadmium content was ten times higher in *Thlaspi*-Viviez than in *Thlaspi*-Prayon.

The quantities of Zn (and Cd, no presented results) exported by *T. caerulescens* increased with N fertilization and particularly with N-nitrate (Figures 3).

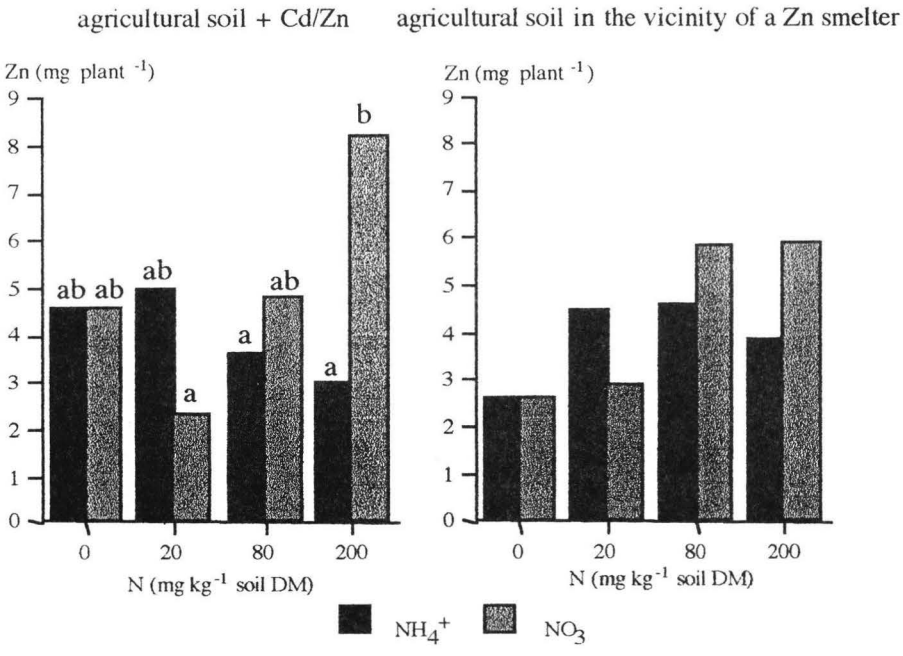

Figure 3. Zn in the aerial parts of *T. caerulescens* as affected by nitrogen fertilization

On a practical point of view, the optimum N fertilization rate permitting the highest biomass production and the highest Zn concentration in the leaves of *T. caerulescens* was 80 mg N kg^{-1} i.e 240 kg N ha^{-1} in two 120 kg ha^{-1} supplies (Table 2). For Cd, the maximum of exportation was allways obtained with the 200 mg N kg^{-1} rate.

Table 2. N fertilization rates optimizing Zn exportation to the leaves of *Thlaspi*

mineral nitrogen form	NO_3^-	NH_4^+
	mg kg^{-1} soil DM	
agricultural soil artificially polluted	200	20
industrial soil	80	80

If the fertilization rates can be oriented by a phytoextraction objective, they have to be environmentally friendly to avoid soil and water contamination by nitrates. Like in agriculture, the dynamic of nitrogen in the soil-plant system seems essential in industrial polluted soils (Yevdokimova, 1994).

Phytoextraction in field conditions

A field experiment on agricultural soil was conducted to assess the impact on hyperaccumulation of different N fertility rates due to added urban sludge. *Thlaspi* responded to N fertilisation. The added urban sludge increased plant biomass and extraction of metals despite a slight decrease in metal concentration in plant tissues in larger plants which was lower than that deduced from the dilution effect. The largest plants contributed mainly to Zn extraction (Figure 4).

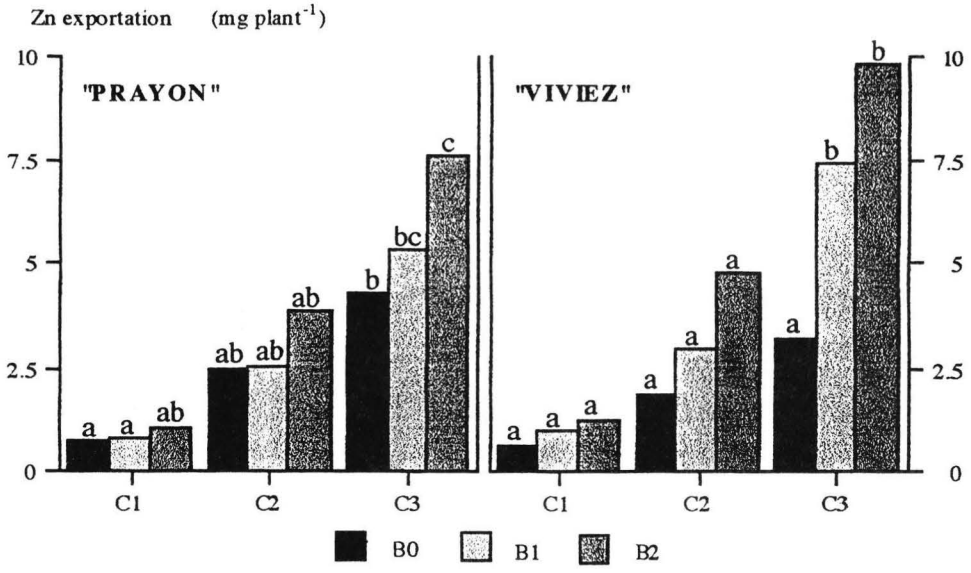

Figure 4. Zinc exportation by the aerial parts of *T. caerulescens* (Prayon and Viviez) according to the dry matter class and the urban sludge rate applied per year during 2 years (B0 : no sludge ; B1 : 3 t ha^{-1} $year^{-1}$; B2 15t ha^{-1} $year^{-1}$) (C1 : ≤ 1 g ; C2 : > 1 g and < 5 g ; C3 : ≥ 5 g)

The contributions of the hyperaccumulating plant *T. caerulescens* and the non-hyperaccumulating, high biomass producing plant *B. napus* to the extraction of metals were very different. In our experimental conditions, *B. napus* was not a candidate for

phytoextraction while *T. caerulescens* considerably reduced Cd and Zn concentrations in soil (Tables 3 & 4).

Table 3. Extraction of zinc by the leaves of *Brassica napus* from an agricultural soil amended with heavy metal rich urban sludge (60 plants m^{-2})

urban sludge rate (t ha^{-1} $year^{-1}$)	3	15
1996-1997	kg ha^{-1}	
quantity of addedZn (1995-1997)	14	70
quantity of Zn exported by *B. napus*	0.14	0.30
number of crops needed to extract the quantity of Zn added from 1995 to 1997	100	233

Table 4. Extraction of cadmium and zinc by the aerial parts of *Thlaspi caerulescens* from an agricultural soil amended with heavy metal rich urban sludge (100 plants m^{-2})

Cd		
urban sludge rate (t ha^{-1} $year^{-1}$)	3	15
1996-1997	g Cd ha^{-1}	
quantity of addedCd (1995-1997)	146	732
quantity of Cd exported by *T. caerulescens* Prayon	2	2
quantity of Cd exported by *T. caerulescens* Viviez	28	61
number of crops needed to extract the quantity of Cd added from 1995 to 1997		
T. caerulescens Prayon	73	366
T. caerulescens Viviez	6	12

Zn		
urban sludge rate (t ha^{-1} $year^{-1}$)	3	15
1996-1997	kg Zn ha^{-1}	
quantity of addedZn (1995-1997)	14	70
quantity of Zn exported by *T. caerulescens* Prayon	2.2	3.8
quantity of Zn exported by *T. caerulescens* Viviez	2.1	4.1
number of crops needed to extract the quantity of Zn added from 1995 to 1997		
T. caerulescens Prayon	7	19
T. caerulescens Viviez	7	17

CONCLUSION

Phytoextraction is the use of hyperaccumulating plants to remove toxic metals from polluted soils. This work was aimed at determining the behaviour and ability to extract metals of the Zn/Cd hyperaccumulator, *Thlaspi caerulescens*, grown on various polluted soils and to assess its response to agronomic practices. Experiments showed very promising results and significant decrease in cadmium and zinc content in soil. *T. caerulescens* plants originated from Viviez exhibited a high potential for Cd and Zn extraction from polluted soil. Nitrogen fertilisation increased plant biomass and extraction of metals despite a slight decrease in metal concentration in plant tissues in larger plants which was lower than that deduced from the dilution effect. However, phosphorus fertilisation had little effect on growth and a slight depression in metal uptake was observed. In conclusion, phytoextraction of metals with selected hyperaccumulators can be improved by adequate agronomic practices which enhanced plant biomass production without reduction of the metal uptake. Successful transfer of phytoextraction from the laboratory to the field is one of our results and forms a crucial step in the development of this technology. Furthermore, adding fertilizers which increase biomass production of hyperaccumulating plants without penalizing metal concentrations can be extremely effective in improving phytoextraction in the laboratory and in the field and can make this process more cost effective. Certain varieties of wild and crop-related *Brassicaseae* are selected for their ability to accumulate metals in harvestable parts but not to hyperaccumulate metals. Under controlled and field conditions we demonstrated that non hyperaccumulating, but high biomass producing species like *Arenatherum elatius* or *Brassica napus* were no effective candidates for phytoextraction. This leads us to conclude that metal hyperaccumulating plants like *T. caerulescens* have to be privileged to attain the objective of phytoextraction.

ACKNOWLEDGMENTS

The authors wish to thank the company Ingérop (Director J. Cercelet), and the *Agence de l'Environnement et de la Maîtrise de l'Energie* (Ademe) for providing a research scolarship to C. Schwartz. They are also indebted to *Lyonnaise des Eaux* (Dr. I. Coulomb) and the *Etablissement Public Métropole Lorraine* (S. Muzika and J. Pierson) for financial support of the research on phytoremediation. The authors are gratefull to Dr. A.J.M. Baker for providing plant material.

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

AFTER-CARE IS MANAGEMENT CARE

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Key words: Data bases, environmental management, groundwater monitoring, landfills, contaminated soil, legislation, computer model, policy, protection, practice.

Summary:

In order to decrease the risk of diffusion of chemical components from landfills, from partly sanitated sites or from infrastructural works with secondary building materials, the City of Rotterdam has established a special organisation to tend to the aftercare. This organisation is subject to prevailing rules and regulations, considers aftercare as part of its regular responsibilities, like road construction, and is established at the old -non legalised- aftercare locations.

Résumé:

Afin de minimaliser le risque de diffusion d'éléments chimiques dans les lieux de déversement, dans la terre contaminée qui a été laissée après l'épuration d'un terrain, ou après des projets civiles avec des matériaux de constructions secondaires, la Ville de Rotterdam a établi une organisation spéciale pour s'occuper de cette matière. Cette organisation est liée aux règles de la municipalité et considère l'accomplissement de ses tâches comme une des charges réglementaires de la municipalité, comparable à la construction de routes. Elle se guide, avec l'aide d'un modéle prioritaire, sur les établissements de ce genre qui -bien qu'elles n'étaient pas légalisées- existaient déjà.

Kurzfassung:

Damit die Diffusionsgefahr chemischer Ablagerungsbestandteile, Bodenverschutzung, die nach Bodensanierung zurückgelassen ist, und Zivilprojekte mit Sekundärbaumaterialien verringert wird, hat die Stadt Rotterdam eine Spezialorganisation gegründet. Die Organisation beruht auf Gesetzen und Regeln, betrachtet die Nachsorge als Gemeindeverwaltung, sowie de Instandhaltung von Strassen, und richtet sich auch, mit Hilfe eines Prioritätsmodells, auf die nicht gesetsmässigen Nachsorgestellen.

Contaminated Soil '98, Thomas Telford, London, 1998, 621–630

1. Introduction

Contamination of the soil entails risks both for man and his environment. Locations where such conditions prevail are, among others, dumping sites, soil sanitation areas containing leftover contaminated soil and large scale redevelopment areas using secondary building materials. Dispersion on the long run has to be controlled. Aftercare is a management concept that can be used to determine and control the risk of environmental contamination by monitoring and by taking civil measures, like isolation, putting in drains and other facilities. In this manner, the next generation should not be burdened with huge environmental damage.
In practice, monitoring is not the only tool for aftercare. It also requires a whole new organisational approach. Aftercare encompasses aspects like function of use, destinations, relationship owner and user, finance, administration, law, geohydrology, toxicology and civil engineering. All these elements have to be integrated into efficient planning and organisation.
Rotterdam plans to realise aftercare for all its existing contaminated locations. It has been established that more than 400 locations have been polluted, comprising old depots, inadequately treated soil sanitation locations and infrastructural works with secondary building materials. As the financial resources are limited, it is not possible to realise aftercare at all of these locations and a model has been developed giving priority to environmentally high-risk projects. At this moment, almost 60 aftercare projects have been realised. The remaining locations will be taken care of over the next few years.
With the data from these projects, Rotterdam intends to create a policy for aftercare not only for existing problem locations, but for possible new cases in the future as well.

2. Problem analysis

The development of the aftercare concept is purely in a technical stage. At present hardly any data are available about aftercare organisations. The City of Rotterdam intends to organise an efficient implementation of aftercare. The question is how and in which way the municipality can best tackle the problem of aftercare for dumping sites, soil sanitation areas, and civil projects using secondary building materials on a large scale. This paper will take a close look at the development of aftercare policy in Rotterdam.

3. Starting points

The definition of the problem touches a number of aspects closely related to aftercare and municipal organisation. In order to create an efficient aftercare organisation it is essential to gain a clear insight into the size and intensity of the aftercare locations, both past and present. The Rotterdam Public Works Department of Environmental Engineering has inventorized the old aftercare locations. Also, a priority model has been developed which can list a priority sequence in order of distribution risk areas, considering the state of the environment. On grounds of experience a target level has been developed defining the technical merits of

aftercare. In more general terms, the following starting-points apply for an efficient aftercare organization:

- connections with an existing internal organisation;
- compliance with the rules and regulations;
- financial and organisational capacity as a guarantee for the implementation of aftercare.

Most management instruments, significant to the Rotterdam aftercare organisation will be expounded in the following chapters.

4. Scope

During the past years, increasing attention has been given to the issue of aftercare. On a national level, the legal obligations for aftercare have been defined for the first time in the previously called Interim-law Soil Sanitation.
From a legal point of view, the City of Rotterdam is responsible for the aftercare of contaminated soil in redevelopment areas and as of 1999 this is also valid for the pollution control of large scale use of secondary building materials as in wind- and soundbarriers. The dumping sites are the responsibility of the province and not the municipality's.
For the municipality of Rotterdam, it is essential that jurisdiction is focussed on present and future soil sanitation projects, for which subsidies have been made available for making diagnosis and taking adequate measures. Long-term management like monitoring, renovation and replacement of supplies is the responsibility of the municipality, comparable to its task of management of public roads and waterways, public space planning and works of art.
Rotterdam also intends to develop a policy for the non-legalized old aftercare locations. This is not only desirable for the potential danger to public health, but also cost-effective and necessary in order to prevent negative publicity and the related political managerial implications if calamaties were to occur.
All this has led to the making of an inventory of the available potential aftercare locations in Rotterdam, based on data in the archives at hand. This inventory is not necessarily complete. Other restrictions are:

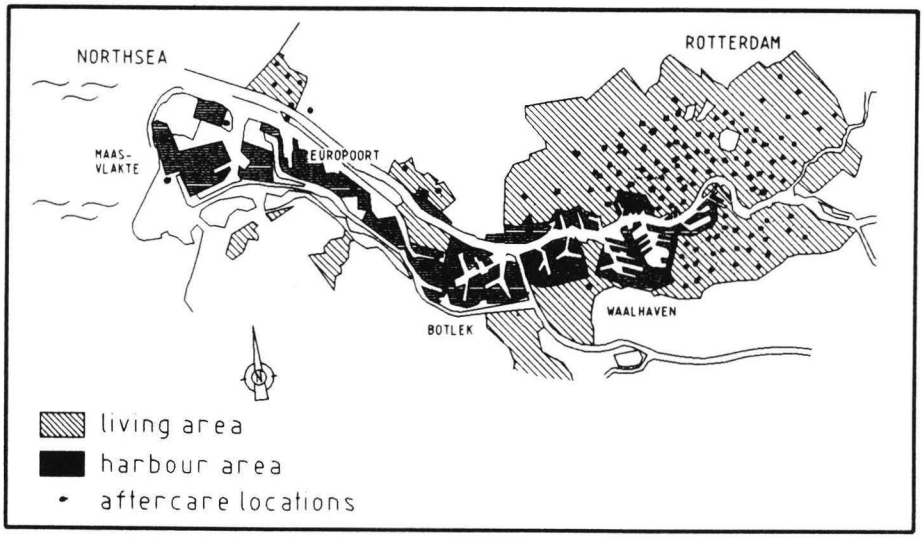
-all deposits of dredgings have been left aside;
-the inventory has been submitted to a number of previous staff members;
-it has not always been possible to determine the status of a location.

All in all the inventory lists: 130 old dumping sites, 5 sites with large scale use of secondary building materials and 236 soil sanitation sites with leftover contaminated soil. Initially, only the topographical data have been listed and put into a database.

The chart below shows an overview of the legal responsibilities of the City of Rotterdam:

	old objects	*new objects*
no statutory regulation	- 130 dumping sites - 200 old soil sanitation sites - 5 large scale secondary building projects	none
by statutory regulation	- 36 soil sanitation sites	- appr. 3-5 future soil sanitation sites a year; - future large scale secondary building projects

The aftercare locations of Rotterdam are showed in the chart below. Remarkable is the higher concentration in the living area.



5. Rotterdam Aftercare policy

The Memorandum Joint Policy Soil Sanitation, as recently formulated by the Mayor and Councilmen of the City of Rotterdam, acts as compulsory framework for the

Rotterdam area.It defines aftercare as follows:
" maintaining isolation measures as applicable at a sanitation site in order to guarantee the quality of the sanitation process and the implied sustainable reduction of risks for public health and environment. Aftercare relates to -among others- maintenance, repair, and replacement of these facilities, supervision to its efficient use (f.i. by monitoring) and the implementation of its applications"

In general, this should be interpreted as meaning the isolation facilities, measures of control as pumping and management of these measures, f.i. by monitoring the groundwater monitoring wells.
The extent of the risk of diffusion and its possible control can only be described after taking a precise inventory of the source, the path and the effect. By source is meant the nature, magnitude and location of the chemical pollution. The path indicates the distance a substance can travel, which is determined by the soil profile and the geohydrology. The effect is the function of the surroundings which could be affected. In practice, data in the field should be collected over a period of a year in order to gain information about the source and the path. Soil samples and data about the quality and rise of the groundwater give a more solid grip on the situation.

Subsequently, a strategy of control and implementation of aftercare is possible.
All in all, the following stages can be distinguished for the approach to aftercare:
1. the initial stage: is aftercare necessary ?;
2. the stage for programming, planning the preparation and implementation;
3. preparation and development of the aftercare project, putting an aftercare plan on paper giving data about locations, the reasons for aftercare, the source, path, effect, measures to be taken, organisation and funding;
4. implementation stage I, providing facilities;
5. looking for facts. Perform measurements over a period of a year. What does the soil actually contain?
6. additional facilities (if necessary) place extra sounding pipes, repair pumps, etc.;
7. adjust the aftercare project;
8. implement the aftercare following the aftercare scheme, implementation stage II.

The basis for aftercare is the aftercare scheme. Except knowledge about the source, path, effect and control measures, it also provides information about funding, legal, organisational and topographical aspects. This clearly demonstrates the multidisciplinary character of aftercare.
In soil policy, a distinction can be made between mobile and non-mobile pollution. Limited aftercare should be sufficient after isolation of non-mobile (leftover) pollution. This should at least include the registration of the (leftover) pollution, repair of possible soil cover constructions or other isolating provisions in case of penetration by digging of these constructions. Apart from that, a change in the function of the soil should be pointed out.
When isolating mobile (leftover) pollution more that usual aftercare is necessary in order to maintain, control, and if necessary replace the isolation-, management- and control- facilities in question. Except the above aspects for non-mobile (leftover) pollution, the following could be relevant:

- maintenance, possible repair and replacement as well as observation of the groundwater monitoring wells;
- regulation and/or monitoring of groundwater levels and rise in waterlevels;
- control, maintenance and possible repair and replacement of barrier- and liner constructions, pumps, water purification- and other installations;
- periodical analysis of ground-, sludge-, groundwater- and airsamples (soil/crawl space);
- testing of the periodical analysis of warning functions and acting in accordance with the agreements made in the aftercare plan in case of exceeding the warning functions;
- periodical reports/evaluation.

Apart from this, aspects like responsibilities, tasks and authorities should be well defined in an aftercare plan. At real estate transactions which concern property under aftercare, these elements will have to be thoroughly regulated during the conveyancing. The individual initiating the transaction of the land in question is duty-bound to inform the other party in all respects. On the other hand, the other party is also responsible for gathering all possible relevant information.

6. Implementation aftercare: state of affairs

Considering the rather recent history of aftercare policy on a provincial and on a national level, the Rotterdam approach is still in a development stage. Acquiring concrete experience with aftercare and related activities started in 1997 with the draft of 35 aftercare projects for statutory soil sanitation locations and one aftercare plan for an old dumping site. The central issue is the redevelopment of these sites. For a whole year, assessments will be made about the nature, location and possible contamination risk of the pollution. Subsequently, evaluations will be made wether additional isolation-, management-, and control arragements are necessary. If the location is carefully prepared, it can be managed, comparable to the management of public roads, works of art, waterways and open space planning.

The approach to the other, non-legalized aftercare locations from the inventory is significant from a point of view of environmental protection, economics and political-management. A well-balanced model has been developed for that purpose: "the priority model". It is not desirable and impossible to organise funding as well as implementation for all potential aftercare locations. In view of an efficient and financial output, it is essential to give priority to a number of aftercare locations, in order to make well-founded choices about the most "aftercare needy" locations (to be called: priority aftercare locations from now on). From this starting point, a first set-up will have to be made to establish provisional priorities for aftercare locations.

In order to determine the priority for aftercare of the locations selected, information should be gathered about the substance, the medium and the surroundings, and the interaction between all three (Source: Ministry of Housing, Physical Planning and Environment ref.3). The piority is determined by the interaction between the source, the path and the vicinity/ the effect. A similar principle is in accordance with the

SanitationUrgencySystematics (ref.4), which can determine the urgency for sanitation. The following elements determine the risk of diffusion and the priority in aftercare:

The source:	kind, concentration, size/load, location, chemical/physical properties (solvability, decomposition, complexity) of the pollution;
The path:	soil structure (lithology, preference circuits), direction and speed of the groundwatercurrents (seepage/infiltration, drop in the isohypse picture), extent of concentration of the pollution;
The vicinity:	description of where possible pollution could end up (nature area, living area, industrial area etc.)

Apart from that, the following aspects can play a role like: compulsory licenses, the recommandation for aftercare by the proper authorities, and aftercare regulation, because these can be deciding factors in deciding wether a location will be included in the aftercare implementation, or could be an aftercare priority.
Taking into account the limited level of details that can be inventorised at each location, only the transport process is included in giving aftercare priority to spreading risk cases. Interaction- and decomposition-processes are being left out of these considerations.

Information, f.i. about the degree of pollution in soil and groundwater, the type of soil synthesis and the presence of management facilities, was available in the archives in only 36 % of all locations. The remainder of the information above is not complete and assumptions have been made on the basis of limited information and expert judgement. If variables are being included for a location on the basis of assumptions, it is noted in the inventory. Using the topographical indications of coordinates X- and Y, a plot of all locations has been made on a surveyable map of Rotterdam. Thus, it is possible to indicate if a location is in a sensitive sector like in a compound of allotment gardens or a less sensitive sector like the Rotterdam industrial area. Environmental protection prioritising of aftercare locations is implemented by giving a scorenumber to a variable. This score is determined by how often a variable occurs. For instance, the higher the concentration, the higher the score. In case of an unknown variable, the mean score will be used. The balance of the scores between the variable is arbitrary. It is possible to simply vary the balance of the scores in the model, which will influence the final result. As only limited use has been made of information from the archives and the scores have been attributed arbitrarily, the pioritising is indicative. The chart below gives an overall view of the variables includes in the priority model:

source	*path*	*surroundings*	*facilities*	*aftercare duty/ recommandation*
- concentration - size of the location - nature of the information* - mobility	- seepage or infiltration - thickness of the top layer** - concentration in the groundwater - direction of the current	- 18 different area zones***	- isolation-, management- and control-facilities****	- this is not included in the priority pattern but is in the inventory.

NB.:

* The nature of the information refers to the most topically relevant report that has been consulted. A detailed report with topical information scores higher than an old report.

** The thickness of the top layer is the amount of clay and peat together down to the first waterholding pack.

*** The following area functions have been scored: building (residential), beach, industrial area, dune, green space, water, sports park, airport, allotment garden, clear land/waste land, cemetary, railroad, agricultural area, motorway, swamp, main road, sediment deposit, square.

**** isolation-, management-, and control-facilities include respectively: damming barriers like liner- and clay barriers, drainage and pumps, groundwater monitoring wells.

In order to make up a score c.q. consideration based on environmental planning, preliminary work has to be done in the database. Clustering has been made according to the type of locations. The locations where aftercare is compulsory or required for obtaining the necessary license, aftercare must be implemented, are being set apart in the database. For the sanitation sites where aftercare is recommended in the sanatation report (for as far as this is known), an annotation will have to be made in the database as well.

To make up a score c.q. consideration based on environmental planning, the following formula is used:

$$P = \frac{\sum source * \sum path}{\sum facilities} + \sum surrounding$$

7 Organisation

Within the organisation of the Municipal Public Works Department, aftercare can be tackled on three levels: strategic, tactical and operational. On each level, a number of departments of the Public Works Department are involved, according to their knowledge, expertise and affinity.

The chart below renders an outline of tasks in headlines:

LEVELS	TASKS
strategic	determine policy, check policy and advise
tactical	coordination, budget management, reportage, communication, aftercare planning
operational	implementation aftercare, reportage, research, expertise

The Rotterdam Public Works Department has approximately 2500 employees, divided into an Engineering Department, Management Open Spaces, Conservation of the Municipality and other services. The Engineering Department has different directions and comprises the disciplines: environment, geotechnique, harbor management, steel- and concrete, public roads and green space, architecture and project management. In this framework and from these disciplines, support will be given to the aftercare services for advise and implementation.
Because of the managerial character of aftercare, Management of Open Space will play a central, coordinating role, and will direct the other, specialised, departments. Planning, budgeting, acquisition and reportage is implemented by the aftercare bureau which is housed with the Management of Open Space. Conservation of the municipality will test compliance with the rules and regulations.

8 Funding

Finances are essential for the implementation of aftercare. It is important to have an insight into all factors determining the costs. As aftercare has an eternal character, it should be possible to devise a strategy which guarantees implementation of aftercare forever.
The costs of aftercare are divided into one-off costs, which include drawing up the aftercare plan and getting the location ready, as well as periodic costs like control assessment and repair, maintenance and replacement of facilities. The risk of damage to facilities and the risk of calamities are being taken into account in the costs. Rotterdam does not choose to provide a fund, but prefers aftercare budgetting on a yearly basis. This will prevent funds being left untouched and capital un-used.
Just like the aftercare policy itself, the financial side of aftercare is also in a development stage.
The Municipality of Rotterdam under financial pressure, has allotted a budget of 3 million guilders to the project, from its investment programme 1996-1999. Part of this has been made available for the implementation of aftercare for 35 old soil sanitation projects and the treatment of contaminated soil after soil sanitation.

The policy for aftercare will necessitate structural funding for the organisation as well as the implementation. Therefor, it is recommended to reserve funding for aftercare from the municipal budget.
It is expected that the workload of the coordinating aftercare bureau will increase during the coming months by the implementation of aftercare for the "new" legalized locations and the "old" non-legalized locations due to the inventory cq. the list for prioritisation.

If aftercare can be put into effect by one organisation only, this will save costs on the total aftercare budget. It might be interesting, in this respect, to undertake aftercare for third parties.

9 Perspective

Intentions are to manage all potential aftercare locations in a structured manner. This means that all relevant aftercare locations on the inventory will be taken care of in succession, conform the priority scheme.
At this moment, a beginning has been made to form an AftercareManagementSystem (in short: AMS). This system aims at gathering relevant aftercare information and storing it, to do the reportage and to point out areas that need immediate action. For instance when the limits of permissible concentration have been exceeded or to indicate when control has to take place.
The AMS can be consulted by all interested parties and can also give information to real estate developers wishing to check on the limitations pertaining to a specific area.
Additional experience and knowledge of existing and new measuring techniques will certainly contribute in a positive way to the implementation of aftercare.

10 Conclusions

The municipality of Rotterdam has realised an aftercare concept and organisation. Beneath environmental risks, this concept requires evenly attention for financial, juridical and organizational aspects.
The municipality of Rotterdam has chosen for financing on a yearly base. The costs of aftercare are included in the municipal budget. The formation of a fund was supposed to be less manageable.
Starting point of the aftercare concept is that all (potentially) contaminated locations are included in the program. A model has been developed to prioritize the environmental high-risk locations.
Starting point for the organization structure is the regular organisation for infrastructural works. The City Council is responsible at strategic level. Public Works, Department of the Management of Open Space plays a coordinating role on tactical level. The operational aspects are being carried out by the Engineering Department.

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Flexible Emission Control, a cost-effective alternative for Isolation

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Summary

In the implementation of (aftercare of) I.C.M. countermeasures (Isolation, Control and Monitoring), many bottlenecks are experienced. These bottlenecks are usually the consequence of the lack of unambiguous concepts, a lack of insight into recurring risks and the misinterpretation of measurements, and also due to the inherent problem of how to interprete soil heterogeneity. This causes unnecessary high costs of remediation and aftercare.

This paper present the results of an inventory of the bottlenecks of aftercare and of the feasibility of a new concept of emission control. With the concept which is called 'Flexible Emission Control' (F.E.C.) a spread over time and a large reduction of costs can be achieved. Managing contaminated sites with this concept means that the control area is extended, monitoring takes place in the flanks and in the contaminated soil and remediation actions are minimalized, but a back-up remediation is designed in advance. The back-up remediation system can be implemented if monitoring measurements exceed certain limits. The time and space that is created are being used for validating migration risks.

We anticipate that a substantial number of the bottlenecks in isolation, control and aftercare, can be made surmountable using the concept, thereby archieving in general a large cost reduction.

Kurzfassung

Bei der Ausführung von Nachsorge einer I.B.C.-Gegenmaßnahme (Isolation, Beheerschung und Kontrolle) werden häufig Probleme unterfunden. Die Probleme verursacht/entstehen als Folge von undeutlichen Konzepten, zu wenig Einsicht in wiederauftretende Risiko's und falsche Auswertung von Meßwerten. Neben dem vor der Hand liegendem Problem von der Auswertung des Bodenaufbaues leitet dies zu hochen Sanierungs- und Nachsorgekosten.

In dieser Publikation werden die Untersuchungsresultaten präsentiert, der Problemerfassung und Eignungsprüfung von einer neuen Methode zur Emissionskontrolle. Mit der neuen Methode, genannt ‚Flexibele Emmisionskontrolle (F.E.C.)', werden die Sanierungs- und Nachsorgekosten verringert und darüberhinaus über einen längeren Zeitraum verteilt. Management von verseuchten

Contaminated Soil '98, Thomas Telford, London, 1998, 631–640

und kontaminierten Standorten mit dieser neuen Methode bedeutet, daß das Kontrollegebiet wird vergrößert, Kontrolle findet am Rand des Kontrollegebietes platz und in der verseuchten Zone. Die Sanierungsmaßnahme wird minimalisiert, während gleichzeitig eine Back-up Sanierungsmaßnahme zur Verfügung steht. Die Back-up Sanierungsmaßnahme kann ausgeführt werden wenn die Meßwerte des Kontrolleprogramms dazu Anleitung geben. Der Zeitwinst, der gebucht wird, kann benutzt werden, um wirklich auftretende Schadstofftransporte und Risiko's im Feld zu verifizieren.

Wir gehen davon aus, daß eine nicht unerhäbliche Zahl Problemen in der Sanierung und Nachsorge, durch Anwendung der neuen Methode nicht mehr Auftreten. Hierdurch werden im algemeinen die Sanierungs- und Nachsorgekosten erheblich reduziert.

Resumé

En effectuant le post-cure des contre-mesures (isoler, maîtriser, contrôler) il se presente beaucoup d'oppressions. Ces oppressions sont le plus souvent (pour la plupart) la conséquence d'une esquisse mal définiée, une manque d'idée claire des risques à attendre et une mauvaise explication des mesurages. Et puis il y a le problème comment à interpréter l'effet d'hétérogénité des sols.
Cet article présente les résultats d'un inventaire des oppressions et la faisabilité d'un nouveau projet de maîtrise d'émission. Avec l'ébauche nommé "flexible emission control" (F.E.C.) une diffusion dans le temps et une grande réduction des frais peuvent être atteintes.
Le maîtrise des sites poluées signifie avec cet ébauche que la localité à maîtriser sera plus vaste et le contrôle aura lieu dans les flancs de la site à maîtriser et que les remèdes seront minimalisés, mais en avant un remède à l'arrière plan a été créé.
Le remède tenu à l'arrière plan peut être effectué quand les mesurages contrôlants dépassent certaines limites. Le temps et l'espace créés sont utilisés pour valider pratiquement les risques de migration.

Nous anticipons qu'une quantité considérable des oppressions du post-cure peut être surmonté en appliquant l'esquisse.

1. Introduction

'Isolation, Control and Monitoring' (I.C.M.) is an approach for contaminated soils - which becomes increasingly popular. It is a reliable solution as long as emissions can be reduced sufficiently and monitored. So aftercare, as an essential part of active soil protection is increasingly important. Aftercare is not only monitoring but the complete set of measures that must be undertaken after finishing the active remediation phase, to assure an optimal control of the site.

In practice, many difficulties are experienced in carrying out aftercare in I.C.M. in practice. Among them is the increasing costs of aftercare. More cost-effective aftercare and moreover a more cost-effective control of emissions, could be helpful in creating a revitalised remediation operation. The objective of the study initiated in 1997 was to develop an effective methodology for isolation, control and aftercare, including an approach in which many of the bottlenecks could be eliminated.

Based on our own experiences in the execution of aftercare we classified the most important bottlenecks as:

- the lack of a clear concept
- difficulties with collation of representative monitoring data and it's interpretation.

In the preliminary investigation (Heijer 1997) the problem-definition was described on a more scientific basis. The study was simultaneously carried out along three tracks:

- An analysis of bottlenecks based on interviews and case-studies
- The development of an innovative concept which makes the bottlenecks more controllable
- Assessing the feasibility of the concept under different situations.

From this study a concept has been developed for a cost-effective alternative: 'Flexible Emission Control'. In this concept the counter measures can be implemented in stages. As an example, expensive counter measures like barriers are only installed after all assumptions related to migration and presumed future impacts are 'validated' with field measurements. So uncertainties will not be translated into unnecessary and overengineered counter measures. As long as isolation is not 'physically' carried out risks are controlled by the monitoring system. The results of the field measurement system can lead to:

- readjusting migration models
- additional measurements
- additional counter measures.

In a follow up study, which is being carried out now, the concept is worked out for

two cases: a landfill (emissions have not taken place yet) and a former pesticides factory (a deep aquifer is already contaminated). In both situations uncertainties have a considerable impact on the decision making process on counter measures and the objectives that must be complied with them. A remediation strategy has been developed with a first stage of monitoring. In this stage emissions are acceptable as long as they are controllable. Only if undesired emissions are proven with monitoring results, more strict counter measures will be taken. If it is found that contaminants will never cause unacceptable problems/damage a monitoring system will suffice and expensive counter measures are not needed. However, it is a prerequisite that all parties can accept the protection that the monitoring system offers.

2. Analysis of bottlenecks

For our study we interviewed consultants, problem owners and authorities. Ten cases were evaluated. The bottlenecks were separated into the stage of the project (investigation, design, installation, aftercare etc.) and their nature: technical, financial, organisational and legal.

In Table 1 a summary is given of the bottlenecks. Many of them have their origin in uncertainties concerning the initial contamination, interpretation of heterogeneity and the representivity of samples.

Table 1 Summary of most important bottlenecks in aftercare:

Bottlenecks	Causes of the bottlenecks
Stage of decision making	
- costs of aftercare cannot be estimated accurately	- how long is aftercare needed?
- zero-emission is not controllable	- what are the consequences of failure?
Designing the remediation	
- establishing the objective of monitoring	- lack of understanding of failure scenarios of the isolation measures - zero-emission is impossible - how to quantify the protection level of monitoring - initial situation and migration processes are not well known - reliability and accuracy of measurements is unknown
- the reliability of the monitoring system is unknown	- lack of a concept
Transfer of a site to another (aftercare) organisation	
- uncertainties about (future) costs	- how long is aftercare needed?
- uncertainties about risk of failure	- zero emission is impossible
- aftercare can not be commanded by law	- aftercare is not sufficiently incorporated intolegislation
During aftercare	
- insufficient systematic approach	- lack of objective and concept for aftercare
- organisation desintegrates with time	- lack of organisation, discipline, plans are not executable, too much effort
- difficulties with interpretation of data	- initial situation unclear, lack of understanding of the dynamics of the system, samples with low representativity, poor understanding of heterogeneity
- not clear when to intervene	- lack of a model for decision-making

3. An innovative concept; 'Flexible Emission Control' (F.E.C.)

Instead of searching for solutions for all bottlenecks they can also be made more 'controllable'. In developing F.E.C. we had four objectives:

- to make uncertainties, especially those due to heterogeneity 'controllable'
- to create the space (spatial and temporal) which is needed to measure and monitor processes so that a sufficiently reliable model of the soil, transport and behaviour (decomposition prognosis), of contaminants can be developed
- to make it possible to remediate if necessary in stages, allowing greater flexibility
- to create an easily implementable monitoring system with clear objectives.

The basic assumption in this approach is that an emission is acceptable as long as it is controllable and can be monitored. This complies with one of the criteria of the Risk Based Corrective Actions (RBCA) approach, that accepts emissions as long as a predefined standard at target locations will not be exceeded, with 85% reliability.

In the F.E.C.-concept the control area is extended up to an artificial line outside the contaminated area. This line is called the *'fail-safe limit'*. It is the outer limit for which a strict emission limit is defined by the authorities. In this area, three sub-areas are present:

- the system-area in which remediation activities take place (the area within the *'system-limit'*)
- the monitoring-area in which measurements and monitoring take place (the area within the *'monitoring limit'*)
- an outer 'back up control area' where intervention measures can be implemented when unacceptable emissions over the 'fail-safe limit' are foreseen based on monitoring (the area within the *'intervention-limit'*).

The position of the limits is shown in figure 1. The F.E.C. concept is particularly applicable in the following situations:

- when there is doubt about the rate of migration
- breakdown of contaminants to less harmful components takes place
- contaminants migrate but never reach unacceptable concentrations at threatened objects due to 'natural attenuation'
- where insufficient money is available for counter measures
- where in the future remediation can be combined with redevelopment of the site
- when cost-effective remediation techniques are not yet available but are expected in the near future.

In figure 1 a maximum emission profile (at worst case conditions) and a minimum emission profile (at most favorable conditions) is shown. When the measured actual emission indicates a future exceeding of the standards set at the *'fail-safe limit'*, additional monitoring, and/or additional remediation measures (intervention), should be considered.

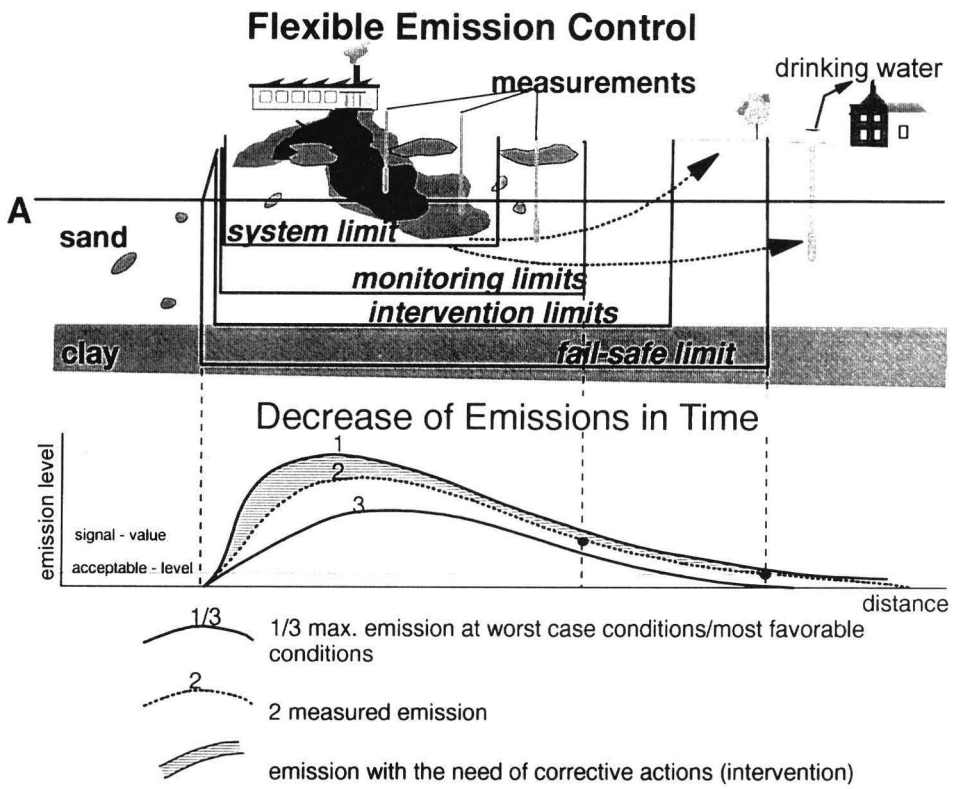

Figure 1 Position of the area limits in the F.E.C.-concept

The most obvious difference with monitoring in the F.E.C.-concept is the fact that measurements are carried out in an area where emissions are allowed. Understanding dynamics of migration is an important aspect in monitoring in the F.E.C.-concept.

Monitoring-measurements in F.E.C. can lead to measures that reduce the migration rate. This in contrast to the I.C.M.-concept in which zero-emission is the objective, with too extensive counter measures as a possible consequence.

4. The feasibility of the F.E.C. concept

The feasibility of the F.E.C.-concept is presently being studied on two cases that are representative for many others in the Netherlands: landfills with preventive isolation measures already present and a former factory of pesticides with groundwater contamination (with halogenated benzines down to 60 metres). In the latter case traditional isolation (I.C.M.) will cost up to US$ 5.000.000,=. The presumed advantages of a flexible and staged approach are:

- combination of remediation with land reclamation and redevelopment of the site in future will save money

- although it is not yet proven, 'natural attenuation' may significantly contribute to a situation in which no standards are exceeded at any threatened objects
- it is expected that in the next five to ten years cost-effective techniques will be developed.

Around the contaminated site an area will be defined in which emissions are acceptable (down to the *fail-safe limit*). In a slightly more restricted area (down to the *monitoring limit)* measurements will be carried out to reduce uncertainties (for example decomposition dynamics of the pesticides) and to monitor migration with the objective of warning when migration starts to exceed the predictions. In that case the in advance designed intervention strategy (within the *'outer back-up control area')* is implemented. The result of this feasibility study will be partly available at the congress.

5. Design of the monitoring network

In the design of the F.E.C.-measures the following steps are distinguished:

- agree upon the position of and the emission limit at the *fail-safe limit* and the required reliability of the system
- describe the migration velocity, plume-morphology and decomposition dynamics of the contaminants
- create an optimal monitoring network; this will mean the optimal combination of positioning the monitoring line and monitoring points (and choice of monitoring instruments) in relation to the risk of failure and the costs of remedial actions.

So the distance from the *monitoring limit* to the *fail-safe limit* is related to the time needed to implement the back-up intervention measures, whenever monitoring data indicate that they are needed.

The monitoring network may be designed with the program called MONICA (Peereboom 1993/1995). In this program a contaminant transport model is coupled with a statistical model (Monte Carlo). On the basis of probability distributions of input parameters the uncertainties in the migration process are taken into account in the calculation of the possibility of detection with the monitoring network. With carrying out numerous simulations, the optimal network (with acceptable chance of failure) can be designed. The MONICA program is used to design the monitoring network for a situation as shown in figure 1.

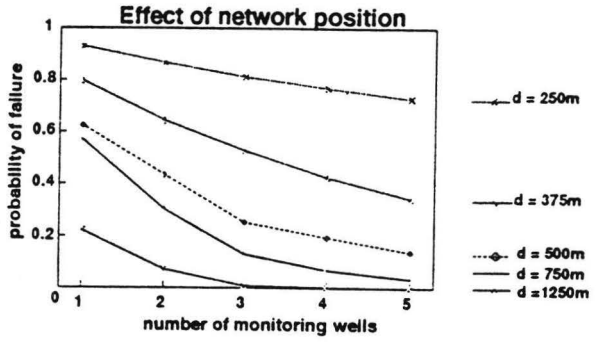

Figure 2 Influence of number of monitoring points on probability of failure with different distances (d) from the monitoring limit to the fail-safe limit

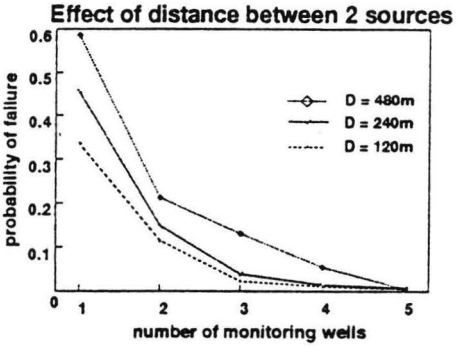

Figure 3 Influence of number of monitoring points on probability of failure in a situation with two contaminant sources and different distances (D) between both contaminant sources

Some examples of simulations are shown in the figures 2 and 3. In figure 2 the influence of the number of monitoring wells on the probability of failure is shown with different distances (d) from the monitoring limit to the fail-safe limit. In figure 3 the effect of the distance (D) between two source zones is shown. With the contaminant transport model, the relation between the acceptable level (see figure 1) at the fail-safe limit and the signal-value at the monitoring line can be given.

6. Conclusions

From this study we conclude that all participants in aftercare experience bottlenecks. These bottlenecks are technical, financial, organisational or legal in nature. The bottlenecks are the consequence of:

- the lack of an unambiguous concept for monitoring, with predefined objectives
- lack of insight into heterogeneity and the effect of it on the interpretation of monitoring data and the prediction of risks
- uncertainties related to monitoring data.

To make the observed bottlenecks more controllable and to reduce remediation costs, an innovative concept is developed. The F.E.C. -concept is based on a more flexible approach to emissions. Emissions are acceptable as long as they are controllable. Therefore one has to start with an extensive remediation stage in which all assumptions on the migration of the contaminants (including natural attenuation) - are 'validated' by monitoring within the contaminated plume in practice and in real time. Subsequently the extensive remediation measures can be intensified until the emission criteria are met. Whenever this turns out to be impossible, the back-up remediation measures can be implemented. In this way unnecessary overdimensioned counter measures can be avoided.

It is shown that a considerable reduction in costs can be achieved through a staged approach with optimal efficiency of the remediation with other activities, and the development of remediation techniques. The availability of a monitoring network with a demonstrable reliability is an absolute requirement.

Acknowledgements

This research is funded by CUR/NOBIS. The objective of NOBIS is to develop, evaluate and demonstrate innovative strategies, methods and techniques which will effectively help to control in-situ remediation by means of biotechnology. This research was carried out with financial help from and in co-operation with the departmental and municipal authorities of 'Provincie Zuid-Holland', 'Gewest Zuid-Kennemerland', 'DCMR Milieudienst Rijnmond', 'Gemeente Utrecht', with the 'Stichting Nazorg Afvalverwijderingsinrichtingen', 'SBNS' and the contractor 'Vermeer Grond en Wegen'. We thank them for their support.

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BUILDING ON CONTAMINATED LAND : THE RISKS

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Key words : building, contaminated sites, risks, landfill gas, remediation, cement-bentonite

SUMMARY

The principal aim of assessing and reducing the risks from contaminants in the ground is often to allow safe building development and re-use of the land. Much of the risk assessment of contaminated land has concentrated on the hazard identification and potential harm to human health. The Building Research Establishment has concentrated on the potential problems of building on or adjacent to contaminated land. This paper describes some of the risks associated with building on contaminated land and in particular research on landfill gas, building materials durability and the performance of containment measures. The aims of each of these three items of research is to develop guidance for those building on contaminated land and develop usable data for risk analysis.

SOMMAIRE

L'évaluation et la réduction des risques représentés par les contaminants dans le sol visent souvent principalement à garantir la sécurité des terrains pour la construction et la remise en valeur. Jusqu'à présent, l'évaluation des risques posés par les terrains contaminés a surtout porté sur l'identification de ces risques et des effets délétères potentiels. Le Building Research Establishment se concentre sur les problèmes potentiels se posant lors de la construction sur un terrain contaminé ou à proximité de celui-ci. Cet exposé décrit certain des risques que pose la construction sur terrains contaminés, et en particulier les recherches effectuées sur les gaz se dégageant des décharges en fouille, sur la robustesse des matériaux de construction et sur l'efficacité des mesures de confinement. Chacun de ces trois axes de recherche vise à permettre de formuler des conseils destinés à ceux qui construisent sur des terrains contaminés et à développer des données utilisables dans le cadre d'une analyse des risques.

ZUSAMMENFASSUNG

Das Hauptziel bei der Bewertung und Reduzierung von durch Bodenkontamination verursachten Risiken ist oft, eine sichere Bebauung und Nutzung des betreffenden Grundstücks zu ermöglichen. Zu einem großen Teil konzentrierte sich die Bewertung der Risiken auf kontaminiertem Land bisher darauf, potentielle Gefahren zu identifizieren und mögliche Gesundheitsschäden aufzuzeigen. Das Building Research Establishment [Einrichtung zur Bauforschung] konzentriert sich auf potentielle Probleme, die in Bauten auftreten können, die sich auf oder unmittelbar neben kontaminierten Grundstücken befinden. Das vorliegende Papier beschreibt einige der Risiken, die mit Bauvorhaben auf kontaminierten Grundstücken einhergehen, und berichtet insbesondere von Forschungsarbeiten zu Gasvorkommen bei Mülldeponien, zur Haltbarkeit von Baustoffen und zur Leistungsfähigkeit einiger Einschließungsmaßnahmen. Jede dieser drei Forschungsrichtungen zielte darauf hin, Leitlinien für das Bauen auf kontaminierten Grundstücken zu entwickeln und nutzbare Daten für die Risikoanalyse zur Verfügung zu stellen.

Contaminated Soil '98, Thomas Telford, London, 1998, 641–650

1. Introduction

The principal aim of assessing the risks and reducing the risks from contaminants (including gas) in the ground is often to allow safe building development and re-use of the land. Much of the risk assessment of contaminated land has concentrated on the hazard identification and potential harm to human health whether by contamination of the water environment, direct ingestion, skin contact, inhalation of air borne contaminants, explosion etc. In recent years the UK government has been developing a framework for contaminated land risk assessment including developing guideline trigger values for contaminants in soil [Ferguson, & Denner, 1994]. Research at the Building Research Establishment (BRE) since 1990 has concentrated on the potential problems of building on or adjacent to contaminated land. This includes the following:

- hazards associated with building on or adjacent to gassing landfill sites and the protection of buildings.
- the performance and protection of building materials in contact with chemically aggressive ground.
- the performance of containment systems.

In each area of research, the objective has been to obtain data, often from real sites, in order to provide guidance on behaviour and performance. It is intended that such guidance will provide the data for more realistic (quantitative) risk analysis.

2. Methane and associated gases

The hazards to buildings and occupiers associated with methane and other gases commonly found with it (principally carbon dioxide) are fairly well understood. However, it is difficult to assign a risk to these hazards because, for example, concentrations of gas in the ground can change by orders of magnitude in a number of hours. It is useful to consider historical data on gas incidents. Such data can be used to try to quantify the scale of the landfill gas problem in the UK [Hartless, 1997]:

- The total number of landfill sites in the UK is approximately 15,000 of which about 6,000 are currently open.
- Surveys of both open and closed gassing landfill sites, in England & Wales in the late 1980's, suggested that 1,006 sites needed gas controls.
- Data on landfill gas incidents is limited, but suggest there have been over 70 recorded landfill gas incidents (1963 - 90), the majority over the last ten years.

Landfill gas incidents can be put into perspective by comparing them to the number of accidental deaths in the UK [Hartless, 1997]. Each year there are approximately 18,000 accidental deaths of which 4,500 occur in the home. Of these, about 100 can be attributed to mains gas inside dwellings; about 60 due to fires and explosions and the remainder due to CO poisoning. The conclusion can be drawn that incidents of mains gas resulting in fire and explosion are rare (risk of death less than one in a million per year), and explosions due to landfill gas are rarer still. This low occurrence has to be balanced against costs of repairing landfill gas explosions, the financial implications of blight and distress to occupiers.

Current guidance and its limitations

The key technical guidance documents that relate to building on gas contaminated sites are Waste Management Paper (WMP) No.27 [DETR, 1991] and BRE Report 212 [BRE, 1991]. CIRIA Report 149 [CIRIA, 1995] summarises current UK practice for dealing with gas contaminated sites. Much of this guidance is focused on assessing the extent of contamination solely on the basis of gas concentrations in the ground. It is widely accepted though that this is inadequate and that information about the quantity or flow of gas from the ground is required to assess the risk [CIRIA, 1995a]. A guide [DETR, 1997] to the design of passive venting systems to disperse gas from beneath buildings has recently been produced which uses both the concentration and the "emission rate" of gas from the ground in order to assess the performance of such systems. Further, WMP26A [DETR, 1994] suggests measurements of gas emissions from monitoring boreholes as an alternative to concentration measurements as a means to assess landfill completion.

A difficulty with this approach is that there is considerable confusion about what is meant by "emission rate" in the context of landfill. Approaches and methods of measuring differ and are generally inadequate. This causes problems when trying to assess the risk of gas contaminated sites.

Hazard ranking and risk assessment

Simple hazard ranking schemes can be used in preference to risk assessment for gas contaminated sites. They are particularly useful when it is necessary to rank a large number of sites in order of priority and where information about them is limited. The scheme used by DETR to allocate resources for its Supplementary Credit Approval (SCA) programme to tackle the problem of closed landfills is based on the distance of a development from a landfill site and the sensitivity of the development [Hartless, 1997].

Refinements to this basic hazard ranking scheme are possible. For example, account can be taken of the age and type of the waste (i.e. its potential to produce gas), the site geology (i.e. potential for gas to migrate) as well as the quantity and quality of gas measurements that have been taken. Each of these relevant factors are broken down into separate categories and given a score. The hazard ranking usually involves adding the scores from each of the factors to give a final score for each site and so all sites can then be ranked in order of priority [Hartless, 1997].

Although, quite simple these types of hazard ranking schemes mimic the "source-pathway-target" approach as used in formal risk estimation. For example, CIRIA Report 152 [CIRIA, 1995b] describes a fault tree approach to estimate the risk of a methane explosion in a house located adjacent to a gassing landfill. Each event that could lead to the ignition of methane within the house (the top event) is considered, e.g. sufficient gas generated at source, failure of barrier to prevent gas migration, movement of gas towards house, entry of gas into house etc. The events are then assigned a probability of failure and so the probability of the top event occurring is simply the product of the individual probabilities.

Similarly, LANDSIM is a software package produced for the Environment Agency that can be used to assess landfill sites using the application of risk assessment to the problem of leachate migration [Environment Agency, 1997]. The program uses the Monte Carlo simulation technique to select inputs for each event randomly according to their probability distribution. The process is repeated many times to produce a probability distribution for the top event that reflects the uncertainty in the system. This is the same process that has been used in the CLEA (Contaminated Land Exposure Assessment) computer model which has been developed to derive guideline values for contaminants in soil [Ferguson, & Denner, 1996]. Such an approach could be used to assign a risk to gas hazards but before this can be done there is a need to develop realistic models of gas movement in and from the ground the ground as well as gas entry into buildings.

The hazard ranking or risk assessment can be used to develop control measures for developments. In the case of development of gas contaminated sites the control measures often take the form of protective measures for buildings, e.g. ventilated suspended floors and gas resistant membranes.

BRE research

BRE has been undertaking research on landfill gas hazards for a number of years with the objective of improving the guidance given in Building Regulations. BRE's landfill gas work has included advice to DETR, measurement and interpretation, and performance of protective measures.

Laboratory and field investigations have shown that rotameters and hot wire anemometers are not suitable techniques to measure flows of landfill gas on site principally because the flows seen on older, less gassy sites are below the limit of detection of these techniques [Hartless, 1995]. Mass flow transducers specifically designed to measure flows of gas from monitoring boreholes are now available. Tests have shown these instruments to be promising but there is a problem with head loss associated with them, i.e. the flow through an uncapped borehole standpipe is greater than when the flow is constrained to pass through narrow bore tubing into the instrument. Comparisons between these instruments and flux boxes to measure landfill gas flow are generally favourable provided the issue of head loss is taken into account. More work in this area is required; in particular there is need to obtain a database of landfill gas flow measurements on a wide range of sites.

On the issue of interpretation of landfill gas measurements, BRE has developed models of landfill gas flow in and around monitoring boreholes, and others that model the effect of meteorological conditions on concentrations and emissions of soil gas. For example, changing atmospheric pressure can greatly influence soil gas movement but the extent of the effect varies with depth and soil permeability. These models need to be developed and once validated against site data can form an integral part of a risk assessment.

BRE has produced guidance on protective measures for new buildings constructed on gas contaminated sites [BRE, 1991]. To test the efficacy of these measures BRE has constructed an experimental structure on a gassing landfill site [Collins, 1995]. Part of the structure is built with a raft foundation above a granular layer with a polyethylene membrane sandwiched between the two. A slotted pipe runs through the granular layer to vent gases to atmosphere. Methane and carbon dioxide levels are monitored beneath the structure and within it. Preliminary results show that the raft appears reasonably effective in excluding gas; when carbon dioxide concentrations beneath the slab are around 30% by volume with the slotted pipe closed the concentrations within the structure were below 0.25% by volume. When the pipe is open at both ends the concentration within it falls to zero rapidly, but concentrations 0.5m away from the pipe fall much more slowly and can take a number of days to reach zero depending on the wind conditions. These results show that passive pipe and gravel systems may not be the most effective way to disperse gas from beneath buildings and this was borne out by computer modelling [DETR, 1997].

Currently, the performance of the suspended floor within the structure is being evaluated. The results of this monitoring exercise will be used to improve the current guidance on gas control measures for buildings and will also play a part in evaluating the risks posed by gas hazards on contaminated sites.

3. Building Materials

Building materials are at risk from attack from many of the contaminants found on contaminated sites. Materials at risk are concrete, mortars, metals, plastics and masonry. This paper concentrates on the risks to cement based materials, in particular concrete. The following aspects are considered:

- contaminants liable to attack the material, and the mechanism of attack;
- the consequences of chemical attack;
- the acceptance criteria determining whether a material can be safely used;
- research to address the areas of uncertainty.

Hazardous contaminants

Materials such as concrete and mortar, which are cement based, are potentially at risk of attack by a number of contaminants. Sulfates, acids and chlorides give rise to concern for both unreinforced and reinforced concrete. However, magnesium, ammonia and phenol are also known to cause deterioration of concrete. It is often said that dense well made concrete is the primary prerequisite for producing durability and there is no substitute for quality of the materials used. However, the inherent chemical properties of the material and the type and form of contamination are just as important.

Sulfates cause deterioration of concrete by reacting primarily with calcium hydroxide and the tricalcium aluminate hydrate phases leading to form highly expansive ettringite phases [BRE, 1991a]. They may also react with calcium silicate hydrate phases in the presence of carbonate ion sources, from aggregates, to form thaumasite [BRE, 1994]. In terms of chemical attack the magnesium and ammonium forms cause

more deterioration than sodium and calcium forms. Both magnesium and ammonium are weak acids which react with the calcium hydroxide in the cement paste. The lowering of the pH in the concrete then causes deterioration of the calcium silicate hydrate phases.

Strong acids cause severe deterioration of concrete of all types by reacting with calcium hydroxide and other phases and leaching material out of the cement paste. Mineral acids and organic acids are known to cause deterioration of concrete. Chlorides are primarily a concern for reinforced concrete where corrosion of the reinforcement can be initiated by the ingress of chloride ions. Although, they also react with calcium aluminate phases in the cement paste to form expansive products. Chloride attack is normally associated with spalling of the cover layer of the concrete as a result of the expansion of the reinforcement.

The consequences of chemical attack on concrete are not easy to assess. Ultimately, chemical attack may cause the collapse of a structure, but such extreme examples are not often found. The more likely scenarios are that some localised deterioration and cracking will occur to the material and result in strength loss. The difficulty of assessing damage when chemical attack occurs below ground is poor accessibility. Damage, when it has been found, has generally been noted to the tops of exposed piles or foundation walls. The form of concrete is important in determining the risks of attack. Slender sections are more at risk of attack in comparison with more massive foundations. Modern housing, which tends to be of lighter construction, should be carefully designed and specified. Slabs and floors on the ground are also more at risk especially where they can dry from the upperside and encourage the movement of contaminants into the concrete from the ground side.

Acceptance criteria for the use of concrete in contaminated sites have not been developed. In most instances the specifier will turn to the recommendations for sulfate soils as defined in BRE Digest 363 [BRE, 1991a]. The recommendations are based on five classes of sulfate concentrations either in the soil or groundwater. As the concentration of sulfate in the soil or groundwater increases the type of concrete changes. This includes increases in the cement content, decrease of w/c ratio and changes in the cement type. As well as sulfates the guidance provides advice on what to do if the soil is acid or contains magnesium (up to 1000 mg/l).

BRE Research

In order to address uncertainties in specification BRE has developed and undertaken a research programme on the suitability of concrete for use in contaminated soils. This has involved, amongst other methods, immersing 100 mm concrete cubes in solutions of contaminants. Nine concrete specifications were used, including the following types: Portland cement (OPC), blastfurnace slag, pulverised fuel ash, sulfate resisting cement (SRPC) and BRECEM [Garvin, & Lewry, 1996]. Of the seven solutions four were based on contamination data in a large number of site investigation reports of typical contaminated sites, two solutions of sodium sulfate based on Digest 363 class 4 levels and a water control.

After one and three years samples of all the materials have been removed from the solutions and subject to tests including compressive strength, chemical analysis and scanning electron microscope studies. The results of the tests have demonstrated that the mixed solutions of contaminants were causing greater deterioration of concrete cubes than sulfate solution alone. Concrete mixes which were found to be of good resistance to the contaminants, for example blastfurnace slag and pulverised fuel ash mixes, were still affected by the solutions through retardation of strength development. This was particularly noticeable over the first year.

The results reported here are interim and the final analysis will be required before definitive conclusions can be reached. However, they tend to suggest that a more conservative approach should be taken, as currently done by some consultants, to concrete specification. This would involve basing concrete specification for contaminated soils on more than just the sulfate levels as currently is the approach used.

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. A former steelmaking plant in North Wales was made available by Flintshire Council. 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.

There has similarly been little research on the performance of other building materials in contaminated land. This includes steel, masonry and plastics which are commonly used in foundations and services. Additional guidance is required for building materials in the form of specific acceptance criteria for a wide range of contaminated land sites.

4. Containment measures

Containment of contamination using physical barriers is an often used remediation method. The intention being to block the pathway between the hazard and the potential targets. Containment methods using in-ground barriers and cover systems are described in detail CIRIA SP 124 [CIRIA, 1993]. BRE research on containment has concentrated largely on assessing the performance of slurry trench cut-off walls using self-hardening cement-bentonite since they are currently the most common type of in-ground vertical barrier used in the UK to control the lateral migration of pollution from contaminated land sites. Typically these cut-off walls are 0.6m wide and less than 12m deep. Approximately 75% of walls constructed in the UK have had a high density polyethylene (HDPE) membrane, usually 2mm thick, placed in the

wall. BRE Digest 395 [BRE, 1994a] and a draft Specification document [ICE, 1996] provide background to construction, materials and specifications.

Cement-bentonite cut-off walls have been in use for more than 20 years and there have been few known cases of unsatisfactory performance. However, there is a lack of in-situ performance data and concerns exist about their performance in chemically aggressive ground in the long term. Questions raised include:

- What is the risk that the barrier will not function as intended for its design life?
- If a malfunction does occur how quickly can it be detected?
- Will a change of use of the site affect the way in which the wall will function?

For a cut-off wall to function satisfactorily as a barrier to leachate migration, the wall must have a reasonably low permeability ($< 1 \times 10^{-9}$ m/s) over its entire length and depth. It must toe-in to an underlying aquiclude to such a depth as to prevent flow underneath the wall. In many cases a cut-off wall is only part of the containment or remediating system and consideration needs to be given to the performance of a whole system and the overall effect on the hydrogeology.

To address some of the uncertainties about the performance of slurry cut-off walls a programme of field and laboratory research is being undertaken. The overall aims of the research work are to facilitate production of improved specifications for construction and validation, increase the understanding on the actual in-situ behaviour and provide industry with data on the long term performance in aggressive ground conditions.

Laboratory studies

Laboratory studies have been undertaken on the set slurry to measure its properties (permeability, strength and stress-strain behaviour) and how they change with time. In particular long term permeation tests in a triaxial cell using site leachates and chemical solutions have been carried out for periods up to one year. At the same time immersion tests have been carried out using similar leachates. The rapid disintegration observed of samples immersed in a site leachate (pH of 2.5, SO_4 = 12000 mg/l) from a gasworks site would imply that cement-bentonite slurry was unsuitable. However, triaxial permeability tests indicated little change of permeability (1×10^{-9} m/s) over a period of a year, except for an decrease in the first 50 days [Tedd, et al, 1997].

In-situ performance

Investigation of the in-situ performance of existing walls has been undertaken at a number of sites. Early work involved coring and in-situ permeability tests on an eight year old cut-off wall (without a membrane) adjacent to an operational landfill site [Tedd, et al, 1995] and the development and assessment of methods to measure in-situ permeability locally in the cut-off walls [Tedd, et al, 1995a]. There are currently no accepted methods of measuring the in-situ permeability in slurry trench cut-off walls. A packer system was developed at BRE for measuring permeability over a discrete length of borehole drilled into an existing wall. Generally the results were an order of

magnitude larger than laboratory measured permeabilities. The use of the piezocone to measure the properties of walls in-situ, particularly the permeability, was assessed at the test site described below [19]. Although satisfactory permeability could not be obtained, variations in strength associated with varying amounts of contaminated soil in the wall could be identified.

The main effort of the research work during the last two years has been to establish a test site at a disused gasworks where elevated levels of sulfate and other contaminants are present at the site and could potentially change the properties of the cement-bentonite. Two boxes have been constructed using slurry cut-off walls, one with a HDPE membrane and one without, to isolate parts of the site. Hydraulic gradients across the walls have been established by pumping into the boxes. The work has shown that the slurry has been contaminated by high sulfate soil. Initially this affected the permeability and strength but the slurry has eventually set to form a low permeability material. These are long term trials and the full value of the experiment will only be realised when the cut-off walls forming the boxes are excavated.

5. Conclusions

This paper has reviewed the risks posed to building on contaminated land with the discussion concentrated on research that BRE has carried out since 1990. The following points can be concluded:

- Human health must be the first consideration when assessing risk of building on contaminated land.
- Other risks include explosion hazard of methane, chemical attack on building materials and uncertainties in the performance of containment measures.
- Research at BRE into these three factors has demonstrated that uncertainties and gaps exist in the current guidance. Further data, being produced through laboratory and field studies, is required before the full range of risks can be assessed and acceptance criteria developed.

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Brownfields versus Greenfield sites under economic and long term environmental considerations

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Key words:
contaminated sites, cost-benefit analysis, costs, ecologial effects, environmental management, industrial areas, remediation, reuse, site restoration,

Summary

The consumption of virgin land (greenfield) in Germany is registered to an extent of 120 ha a day. Approximatly this size of land is sealed every day for building purposes and thereby not anymore available for ecological functions of the soil. At the same time, enough brownfield sites are available for development . This indicates that there is a kind of competition between greenfields and brownfiels with respect to attract investors for the development of land. In other words, old industrial sites have to compete with greenfields and the benefits they offer for potential investors. Thus, the Federal Environmental Agency in Germany has contracted an expertise on land management and on land development procedures comparing and evaluating both, the development of brownfield sites and the development of greenfield sites. The results of this project will be presented.

Zusammenfassung

Der Landschaftsverbrauch in Deutschland beträgt ca. 120 ha pro Tag. Böden auf Flächen dieser Größenordnung werden im Rahmen der Gewerbeflächenerschließungs- oder anderer Baumaßnahmen auf der Grünen Wiese versiegelt und damit dem Naturhaushalt entzogen. Gleichzeitig stehen eine Reihen von Brachflächen zur Sanierung und gewerblichen Erschließung bereit, die nicht angegangen werden. Insoweit besteht in gewisser Weise eine Konkurenzsituation zwischen der Erschließung von Brachflächen und der Erschließung von Naturflächen auf der Grünen Wiese. Das Umweltbundesamt hat zur näheren Untersuchung und Bewertung dieser Flächenerschließungsvarianten einen Forschungsauftrag vergeben. Die Ergebnisse aus dem Vorhaben werden vorgestellt.

Contaminated Soil '98, Thomas Telford, London, 1998, 651–660

BACKGROUND

In the Federal Republic of Germany around 120 ha of ground not built-up is claimed daily for the erection of buildings. The availability of areas for commercial and industrial settlements is restricted at present, as a general rule, to the specification of natural areas. Regardless of the obvious disadvantages of such greenfield sites, as a rule outside community areas, without infrastructure-service access, and the environmental burdens associated with the development by progressive land consumption, the practical realisation of extra-municipal industrial estates and shopping centres shows that these areas indeed meet acceptance on the side of the investors.

The reason for this state of affairs is primarily that those making the decisions for communal area usage are primarily guided by business economic principles. The investors follow the entrepreneurial commerce maxim of optimising profits. The decision routines of the communities are mainly stamped by efforts for new settlement of commercial enterprises and the creation of further employment.

In front of this backdrop, the Federal Environmental Agency [Umweltbundesamt] have awarded a research and development project to a working party of the focon Ingenieurgesellschaft, Aachen and WCI, Wennigsen companies. The objectives of the R+D project, entitled *Contaminated Land Remediation as Basis for the Development of Free Spaces and Assessment of the Development Variants* was to carry out a comparison of the free space development variants, during which both all possible decision relevant factors under consideration for the development of reclaimed abandoned locations, and for the development of green field open spaces be gathered together and assessed. This assessment should not only contain the economic evaluation model on the side of the investors and on the side of the communities. In particular, an attempt should also be made to define a comparative yardstick in terms of the interests of society as a whole for the ecological estimation of these development forms from long-term points of view, including the monetary aspects of the environmental effects.

Assessment Approach

The fundamental logic of the assessment approach developed consists of transforming into a working operation the complex field of decision making on land surface exploitation by quantifiable criteria.

With this objective in mind, the assessment approach contains three material assessment blocks, these being

- the site potential, documenting the communal quality of a land area for commercial settlement through criteria such as size, construction work suitability, connection to the infrastructure etc., and thus illustrates the suitability for reinstatement or for first instatement in the interests of the community,

- the exploitation potential, by means of which the usefulness (advantages of use) in the interests of the investors is measured for example through criteria such as position quality, exploitation restrictions, credit viability etc.,

- the value of the site, which quantifies the ecological, municipal and regional structure value, and beyond this, the "without case" (initial situation without new or first use measures) as well as the "with case" (target situation with new or first use measures),

and additionally a cost-field documenting

- the costs of the area preparation work, which also documents any possibly occurring remediation costs in formerly used areas, as well as the sales revenues aimed for.

Since economic aspects have dominated so far in decisions of this kind, whereas the social determinants were rather viewed as marginal, considerable relevance is attached to assessment of the ecological, municipal and regional structure criteria in the present approach, in order to make the decision on green field settlement, or the alternatives on wasteland - above all dependent on how far the conservation requirements of the non-renewable and limited resource "land", in the sense of the "sustainability" demanded - can be taken into account.

Site Potential as a Representation of Communal Interest

In terms of its equipment and position, every location exhibits a certain reinstatement or first instatement suitability, which is designated as its site potential. The site potential essentially illustrates the community interest structure; it is described by the criteria

- size of the area (criterion 1.1, criterion weighting 3 %),
- construction work suitability of the area (nature of the subsoil) (criterion 1.2, criterion weighting 15 %),
- time available (settlement maturity of the area) (criterion 1.3, criterion weighting 9 %),
- connection to the supply and disposal system/technical infrastructure (criterion 1.4, criterion weighting 19 %),
- connection to the local road traffic network (criterion 1.5, criterion weighting 46 %),
- connection to the public transport network (criterion 1.6, criterion weighting 8 %).

As site potential in the sense of the instatement suitability, the "initial situation" of the location is judged. According to this, any possible changes resulting from the area preparation work are not taken into account in the quantification of the location potential. From the communal point of view, the criteria whose non-fulfilment by the location circumstances would produce the greatest investment needs are of paramount importance. For this reason, the three criteria describing the development are clearly more heavily weighted in the sum than the criteria "size, construction work suitability and availability", although in this respect it also plays a part that the size of the area on hand can only be changed to a limited extent as a rule by additional investments.

For the criterion specific assessment of the location situation, a five level interval scale is used over the spectrum of +4 to 0 (zero point and benefit-unit can be chosen freely; the numerical differences represent the benefit-differences), where an assessment of +4 exhibits an optimal instatement suitability.

Exploitation Potential for Substantiating the Interest of the Investor

From the investor's point of view, every location possesses a more or less high fundamental suitability for its secure exploitation as a commercial location. This basic suitability, designated as exploitation potential, is represented by the following attributes:

- traffic links (accessibility of the area from an autobahn connection) (criterion 2.1, criterion weighting 24 %),
- position quality (degree of centralisation with regard to the supply situation) (criterion 2.2, criterion weighting 17 %),
- opportunities and restrictions of reuse(criterion 2.3, criterion weighting 22 %),
- planning and official approval conditions (criterion 2.4, criterion weighting 14 %),
- liability protection and credit viability (criterion 2.5, criterion weighting 15 %),
- attractiveness/image (criterion 2.6, criterion weighting 8 %),

The exploitation potential chiefly reflects the investor's demands on locations, which is why features ensuring optimal exploitation from the investor's point of view flow into the assessment. Assessment relevant is the "afterwards situation", in other words the exploitation possibilities opened by the location after the implementation or introduction of the necessary preparation work, which in the case of abandoned locations may include any necessary remedial action

General location demand profiles from industry and commerce record that optimal traffic connections, good position quality and exploitation free of restrictions are part of the central demands of the investors. Alongside this, the current pollution discussion presses the question of liability protection, both against the background of the insurance required as well as the necessary credits, into the foreground of investor requirements.

As for assessment of the location potential, a five level scale with the range of +4 to 0 is also used for assessment of the exploitation potential features. With an assessment of +4, the investor demands are very well met, whereas with an assessment of 0 no appreciable exploitation suitability exists.

Site Vaue for Specification of the Demands of Society

The third significant assessment range is the quantification of the site value. The site value contains evaluation of the ecological as well as the municipal and regional structure area functions, and thus represents the environment-policy/social context of the land availment. Since the ecological area functions, as opposed to the municipal and regional structure features in the assessment blocks "site potential" and "exploitation potential", are clearly under-represented in terms of the texture of interests shown, the ecological conditions in "location quality" are represented, in the sense of the inter-subjectivity sought after, by 8 criteria, the municipal structure points of view by 4 criteria, and the regional function correlation by 2 criteria.

For the quantification of the ecological quality, the functional zones "soil", "water", "air/climate" and "habitats" are taken into account as attributes and further differentiated to quantifiable criteria.

Under the viewpoint of the "soil" attribute, the natural functionality of the of the soil is represented by the criteria

- soil structure (criterion 3.1, criterion weighting 13 %),
- topography/relief (criterion 3.2, criterion weighting 4 %), and
- soil quality (criterion 3.3, criterion weighting 18 %).

The functional zone "water" is reflected by the criteria

- ground water re-formation rate (criterion 3.4, criterion weighting 9 %), and

- ground water quality (criterion 3.5, criterion weighting 2 %),

where the natural level is used as an assessment yardstick in each case.

For the functional zone "air/climate", in the sense of the climate regulating equalising potential, the criteria

- quality of the surface area for air diffusion/exchange (criterion 3.6, criterion weighting 1 %), and
- quality of the surface area as a fresh and cold air generation zone (criterion 3.7, criterion weighting 12 %),

are applied.

The biotope quality (criterion 3.8, criterion weighting 9 %) of the locations is represented by the natural state of the biotypes present and their surface proportions.

For the quantification of the urban development and regional structure quality of the locations, the criteria

- municipal functionality of the location (criterion 3.9, criterion weighting 14 %),
- functionality of the interwoven connections (criterion 3.10, criterion weighting 7 %),
- municipal structure and functional further effects (criterion 3.11, criterion weighting 1 %),
- town and countryside image (criterion 3.12, criterion weighting 9 %),
- functionality of the location in the regional correlation structure (criterion 3.13, criterion weighting 4 %), and
- homogeneity of the settlement structure (criterion 3.14, criterion weighting 7 %),

are taken into account.

Assessment of the site takes place via a five level assessment scale between +2 (maximum quality) and -2 (minimum quality); only integral number assessments are allowed. Because of their only limited differentiability, for the criteria "topography/relief", "groundwater re-generation rate", "air exchange quality" and "fresh and cold air generation", the assessment scale is restricted to 3 levels (+1 to -1). The assessment regulations are thus formulated such that both the initial situation ("without case") and the target situation ("with case") can be judged, i.e. the same assessment grid applies to both assessment variants. In this way, the possibility exists of recording the changes in both the ecological and in the municipal and regional structure quality directly, and documenting them as a quality delta.

Illustration of the Integral Benefit by Preference Index (PI) and/or Resulting Monetary Value (RMW)

In order to picture the integral benefit related to the costs, in terms of the assessments carried out, the preference index is worked out; it relativises the benefits determined in points dividing them by the costs, which are quoted as specific costs in DM/m². This means that the preference index has the dimension points per DM and square metre. The alternative to be preferred in each case for the commercial settlement is the one with the highest preference index PI.

Taking into account

- the criterion weightings g for the criteria of the site potential,
- the criterion weightings n for the features of the exploitation potential,
- the criterion weightings w for the criteria of the site value,

as well as including the relevance factors for the location potential (2.5), the exploitation potential (1.0) and the location quality (6.5) in the calculation, the preference index is derived from

$$PI = \frac{(2.5 \times \Sigma g \times SP + 1.0 \times \Sigma n \times NP) + 6.5 \times \Sigma w \times \Delta}{(AK + SK) - VE},$$

where SP is the point assessment of the site potential, NP the point assessment of the exploitation potential and Δ the point assessment of the site value (note the algebraic sign) resulting from the before/after viewpoint, whereas AK represents the preparation work costs, SK the possible remedial action costs for brownfield sites, and VE the sales proceeds to be aimed for.

The assessment system developed has been applied to two concrete examples in Lübeck as an example. These were:

⇒ The greenfield site of "Roggenhorst",
which, in order to retain its economic strength and secure competitiveness in the face of other communities, was developed by the Hanseatic city of Lübeck as a commercial estate; the "Roggenhorst" region represented the sole short and medium-term opportunity for offering commercially developable land with a direct link to the autobahn; the development area with a total of around 76 ha provides a share of 48 ha building land, as well as

⇒ The brownfield site "Metallhüttengelände [Metallurgical works terrain]"
which in Lübeck not only represented the most heavily polluted area of the state of Schleswig-Holstein, but also the largest contiguous piece of land for commercial and industrial exploitation of the Hanseatic city; essential production fields from

1905 were the production of coke from coal, and iron smelting from iron ores; in the course of time a series of additional enterprises completed the production range, their erection primarily serving the processing of recyclable materials; distinguished from one another are essentially the works site (72 ha) and the former slag heap area (10 ha).

Fig. 1 documents the calculation procedure for determining the preference indices.

It can be read from the data that both area variants are different in site potential (e.g. greenfield site Roggenhorst: SPI [site potential index] = 2.3; brownfield site Metallhüttengelände: SPI = 3.64), so that the disused industrial location displays better fundamental suitability from the communal point of view; this tendency is reversed in terms of the exploitation potential from the viewpoint of the investors, where the natural area of Roggenhorst exhibits an exploitation potential index [NPI] of 3.7, whereas the Metallhüttengelände only attains an index of 2.79. To summarise the assessments of site potential and exploitation potential, the Lübeck examples

- Greenfield site: SPI + NPI = 2.43 + 3.7 = 6.13
- Brownfield site: SPI + NPI = 3.64 + 2.79 = 6.43

show that both area-alternatives possess well comparable overall suitability for commercial area allocation.

In contrast to this result, there is a clearly more favourable difference between preparation work, remediation costs and sales revenues for natural areas, which unequivocally speaks against preparation of the brownfield. This implies that the natural area represents the preferred instatement alternative, solely by viewing the site and exploitation potential. This preliminary estimate corresponds to today's practice in many cases.

By including the site value, however, the overall assessment changes decisively. As may be deduced from the data fields on site value, the brownfield site frequently exhibits a positive quality delta as a consequence of the instatement, whereas the greenfield site is mainly judged negatively. This is summed up, e.g. for the natural area of Roggenhorst, by a site value index related to the delta of -1.57, whereas the positive changes for Metallhüttengelände provide a figure of +1.22 (cf. Fig. 1).

By including the relevance factors in the calculation, as well as by reference to the specific costs, the preference indices can determined as

- Greenfield site Roggenhorst:
  PI = (6.075 + 3.70) + (– 10.21) / (39.36 + 0.00) – 46.20 = + 0.066

- Brownfield site Metallhüttengelände:
  PI = (9.1 + 2.79) + 7.93 / (13.33 + 137.09) – 44.88 = +0.188

Site potential 2.5			Area I (Greenfield)		Area II (brownfield)	
No.	Criterion	g	Points SP	g × SP	Points SP	g × SP
1.1	Area size	0.03	+3	+0.09	+3	+0.09
1.2	Construction work suitability	0.15	+1	+0.15	+3	+0.45
1.3	Time available	0.09	0	0.00	+2	+0.18
1.4	Connection to the supply and disposal system	0.19	+1	+0.19	+4	+0.76
1.5	Connection to the traffic network	0.46	+4	+1.84	+4	+1.84
1.6	Connection to the public transport system	0.08	+2	+0.16	+4	+0.32
	SPI = Σ g × SP			+2.43		+3.64
	Relevance value: 2.5 × Σ g × SP = RSP			+6.075		+9.1

Exploitation potential 1.0			Area I (Greenfield)		Area II (brownfield)	
No.	Criterion	n	Points NP	n × NP	Points NP	n × NP
2.1	Connection to the traffic network	0.24	+4	+0.96	+3	+0.72
2.2	Position quality	0.17	+4	+0.68	+4	+0.68
2.3	Exploitation opportunities/restrictions	0.22	+4	+0.88	+2	+0.44
2.4	Planning and official approval conditions	0.14	+3	+0.42	+4	+0.56
2.5	Liability protection and credit viability	0.15	+4	+0.60	+1	+0.15
2.6	Attractiveness/ Image	0.08	+2	+0.16	+3	+0.24
	NPI = Σ n × NP			+3.70		+2.79
	Relevance value: 1.0 × Σ n NP = RNP			+3.70		+2.79

Site value 6.5			Area I (Greenfield)				Area II (brownfield)			
			SW				SW			
No.	Criterion	w	prior	after	Δ	w × Δ	prior	after	Δ	w × Δ
3.1	Soil structure	0.13	+2	-1	-3	-0.39	+2	+2	0	0.00
3.2	Topography/relief	0.04	+1	-1	-2	-0.08	-1	-1	0	0.00
3.3	Soil quality	0.18	+2	+1	-1	-0.18	-2	-1	+1	+0.18
3.4	Groundwater re-generation	0.09	+1	-1	-2	-0.18	-1	-1	0	0.00
3.5	Groundwater quality	0.02	+2	+1	-1	-0.02	-2	0	+2	+0.04
3.6	Air exchange quality	0.01	+1	-1	-2	-0.02	-1	-1	0	0.00
3.7	Quality of cold and fresh air generation	0.02	+1	-1	-2	-0.04	-1	-1	0	0.00
3.8	Biotope quality	0.09	+2	-2	-4	-0.36	-2	-2	0	0.00
3.9	Functionality	0.14	+1	+2	+1	+0.14	-1	+2	+3	+0.42
3.10	Functionality interwoven zone	0.07	+1	+1	0	0.00	-2	+2	+4	+0.28
3.11	Municipal structure additional effects	0.01	0	0	0	0.00	0	0	0	0.00
3.12	Town and landscape image	0.09	+2	-1	-3	-0.27	0	0	0	0.00
3.13	Functionality in the region	0.04	+1	+2	+1	+0.04	-2	+2	+4	+0.16
3.14	Homogeneity of the settlement structure	0.07	+2	-1	-3	-0.21	-1	+1	+2	+0.14
	SWI Δ = Σ w × Δ					-1.57				+1.22
	Relevance value: 6.5 × Σ w × Δ = RSWIΔ					-10.21				+7.93

Area preparation work costs	AK [DM/m²]	39.36	13.33
Remediation costs	SK [DM/m²]	0.00	137.09
Sales revenues	VE [DM/m²]	46.20	44.88
Preference index	$PI = \frac{(RSP + RNP) + RSWI\Delta}{(AK + SK) - VE}$	+0.066	+0.188

Fig. 1: Assessment tableau on the qualitative-quantitative area assessment; example areas Lübeck

Site potential		Roggenhorst		Metallhüttengelände	
		Area I (Greenfield)		Area II (Brownfield)	
No.	Criterion	SP [DM/m²]		SP [DM/m²]	
1.1	Area size	4.50		4.50	
1.2	Construction work suitability	9.00		27.00	
1.3	Time available	0		10.50	
1.4	Connection to the supply and disposal system	11.25		43.00	
1.5	Connection to the traffic network	111.00		111.00	
1.6	Connection to the public transport system	10.13		20.30	
	Sum : Σ SP		145.90		218.30

Exploitation potential		Area I (Greenfield)		Area II (Brownfield)	
No.	Criterion	NP [DM/m²]		NP [DM/m²]	
2.1	Traffic links	30.00		22.50	
2.2	Position quality	21.00		21.00	
2.3	Exploitation opportunities/restrictions	21.00		14.00	
2.4	Planning and official approval conditions	13.50		18.00	
2.5	Liability protection and credit viability	19.00		4.75	
2.6	Attractiveness/ Image	3.00		7.50	
	Sum: Σ NP		116.50		87.75

Site value		Area I (Greenfield)			Area II (Brownfield)		
		SW [DM/m²]			SW [DM/m²]		
No.	Criterion	prior	after	Δ	prior	after	Δ
3.1	Soil structure	+45.00	-22.50	-67.50	-45.00	-45.00	0
3.2	Topography/relief	+6.50	-6.50	-13.00	-6.50	-6.50	0
3.3	Soil quality	+64.00	+32.00	-32.00	-64.00	-32.00	+32.00
3.4	Groundwater re-generation	+16.00	-16.00	-32.00	-16.00	-16.00	0
3.5	Groundwater quality	+7.40	+3.70	-3.70	-7.40	0	+7.40
3.6	Air exchange quality	+2.00	-2.00	-4.00	-2.00	-2.00	0
3.7	Quality of cold and fresh air generation	+5.62	-5.62	-7.24	-5.62	-5.62	0
3.8	Biotope quality	+30.00	-30.00	-60.00	-30.00	-30.00	0
3.9	Functionality	+24.00	+48.00	+24.00	-24.00	+48.00	+72.00
3.10	Functionality interwoven zone	+12.50	+12.50	0	-23.00	+23.00	+30.00
3.11	Municipal structure additional effects	0	0	0	0	0	0
3.12	Town and countryside image	+30.00	-15.00	-45.00	0	0	0
3.13	Functionality in the region	+6.50	+13.00	+6.50	-13.00	+13.00	+26.00
3.14	Homogeneity of the settlement structure	+23.00	-11.50	-34.50	-11.50	+11.50	+23.00
	Sum: Σ SWΔ	+270.52	+2.08	-268.44	-248.02	-37.62	+210.40
	Variant delta (wasteland-natural area)			+478.84			

Area preparation work costs	AK [DM/m²]	+39.36	+13.33
Remediation costs	SK [DM/m²]	0	+137.09
Sales revenues	VE [DM/m²]	+46.20	+44.88
RMW = (Σ SP + Σ NP) + Σ SWΔ - (AK + SK) + VE		+0.89	+410.91

Fig. 2: Monetary assessment of the location alternatives in Lübeck

thus providing evidence of the precedence of the brownfield which, on account of the instatement for commercial exploitation with respect to the pre-determined interest structure, anticipates a clearly higher benefit per cost unit.

More concise and also easier to reconstruct than the qualitative-quantitative assessment, the monetary assessment can show the instatement suitability of alternative areas since it is not derived from dimensionless point assessments combined with amounts involving dimensions, but rather, all criteria are available in monetary form with the dimension DM/m². This opens the possibility of directly offsetting in such a way that from the monetary data determined in the named assessment zones the resulting monetary value (RMW) of the areas is deduced from the projection

$$RMW = (\sum SP + \sum NP) + \sum SW\Delta - (AK + SK) + VE \ [DM/m^2],$$

and the area instatement alternative is to be preferred which exhibits the the highest resulting monetary value (RMW).

The rated practical example from Lübeck provides evidence (cf. Fig. 2) that brownfield recycling represents the clearly better alternative. Whereas the resulting monetary value of Metallhüttengelände is +410.91 DM/m², above all on account of the large positive change of the site value, an RMW of only +0.80 DM/m² is documented for the greenfield area Roggenhorst on account of the clearly negative quality delta of the site value. This means that for Roggenhorst a higher ecological as well as municipal and regional structure value would be essentially destroyed by commercial exploitation, whereas for Metallhüttengelände a disused socially-compatible benefit, represented by the negative site value of the present situation, can be positively activated to such an extent that despite inclusion of the reinstatement costs a very high resulting monetary value can be achieved.

Reference

Forschungs- und Entwicklungsvorhaben 203 40 119
Abschlußbericht
Revitalisierung von Altstandorten versus Inanspruchnahme von Naturflächen - Gegenüberstellung der Flächenalternativen zur gewerblichen Nutzung durch qualitative, quantitative und monetäre Bewertung der gesellschaftlichen Potentiale und Effekte
ARGE focon/WCI im Auftrag des Umweltbundesamtes
Oktober 1997
(english publication in preparation)

Where there is Muck, there is Gold!
Encouraging private investment in derelict and contaminated land

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Key Words: authorities, contaminated soil administration, decontamination, environmental policy instruments, landfills, legislation, liability, redevelopment, remediation, responsibility, sustainability, treatment policy.

Summary

This paper considers the potential for regenerating derelict and contaminated sites in England. It considers the type and extent of dereliction, and how this is likely to change over time. It sets out English Partnerships' approach to public investment in the land reclamation process. Based on the Agency's experience over the last five years, the paper identifies some of the main barriers to attracting private investment in the remediation process. Drawing on the work of the Brownfield group, the paper suggests some possible financial mechanisms for overcoming these barriers. Finally, the paper provides a few examples of English Partnerships' recent successes.

La régénération du partimoine foncier : une idée en or
Encourager l'investissement du secteur privé dans les sites désaffectés et contaminés

Résumé

Cet exposé a pour objet le potentiel de régénération des sites industriels désaffectés et contaminés en Angleterre. Il examine les defférents cas de figure en la matiére (nature du site, degré d'abondon...) et réfléchit aux possibilités d'évolution furure. Il entend expliquer comment *English Partnerships* aborde le probléme de l'investissement du secteur public dans le processus de reconversion du terrain. Sur la base des expériences menées par cette agence au cours des cinq dernières années, l'exposé identifie quelques-uns des obstacles principaux à l'investissement privé dans le processus de réhabilitation. Faisant appel aux travaux du *UK Brownfield Group,* il propose des mécanismes financiers pour surmonter ces obstacles et fournit pour terminer quelques exemples récents des projets menés à bien par *English Partnerships.*

Contaminated Soil '98, Thomas Telford, London, 1998, 661–670

Dreck und Geld liegen beinahe beisammen! Förderung von Privatinvestitionen in dereliktes und kontaminiertes Gelände

Zusammenfassung

Diese Abhandlung beschäftigt sich mit dem Regenerationspotential von dereliktem und kontaminierten Gelände. Sie erwägt die Art des Verfallens und wie weit der Verfall fortgeschritten ist und wie sich das mit der Zeit ändern wird. Sie beschreibt, wie die Agentur, English Partnerships an das Problem der Investitionen durch öffentliche Gelder beim Rückgewinnungsverfarhren dieser Gelände herangegangen ist. Die Adhandlung identifieziert manche der Haupthindernisse, die die Agentur in den letzten fuenf Jahren bei Ihrem Bestreben erlebt hat, Interesse an Privatinvestitionen bei diesem Aushandlungsprozess zu erwecken. Unterstützt durch die Arbeit des 'UK Brownfield Group' macht die Agentur Vorschläge, mÖgliche finanzielle Mechanismen zur Bewältigung dieser Hindernisse einzusetzen. Zuletzt liefert die Abhandlung einige Beispiele von Erfolgen, die die Agentur 'English Partnerships' neulich erlebt hat.

'Where there is muck, there is gold!'

Encouraging private investment in derelict and contaminated land

Jon Rouse and Justin Murphy, English Partnerships

Introduction

For those readers who do not recognise the quotation, or are more familiar with an illusion to 'brass', the adage that 'muck' and 'gold' go together, comes from the French C19th essayist and philosopher, Baudelaire. And he, more than most, would have recognised the wisdom in his words. Located in Paris, Baudealaire witnessed the transformation of his city as Napoleron and Haussman tore down the slums and drove great boulevards through the heart of the medieval city. This reconstruction of Paris is renowned was a work of great urban planning but it can also be characterised as an early recognition of the potential and value of brownfield, and in many cases, contaminated land.

Here in England, in the 1990s we are re-learning the importance of our brownfield land, much of which is contaminated as result of previous industrial use. In the summer of 1996, the UK Town and Country Planning Association published a report - 'The People - Where will they go ?' It revealed the scale of the housing pressures facing the UK at this time. It estimated that an additional 4.4 million households would be looking for homes before the year 2016 in England alone, as a result of various demographic changes, including a rise in the elderly population and single parent family households.

Fifty years ago, the answer to projected population growth and increasing industrial needs was to build satellite towns in the countryside. There was opposition then to such a policy, but that opposition was of naught to the resistance that faces the planners of the 1990s. Every further intrusion into the British countryside will be contested, often with prolonged public protest. Therefore, while in 1940 we were looking outwards, now we must look inwards, to our existing urban settlements and our derelict, contaminated and disused brownfield sites to meet our development needs.

It was for this reason that in 1993 the UK Government decided to create one national Agency for England to take responsibility for promoting the redevelopment of brownfield land. Operating through six regional offices, with a staff team of about 450 and an Investment Fund of over £300 million per annum, our statutory remit is to bring derelict, contaminated, vacant and under-used land back into beneficial use, concentrating on areas of economic and social need. Our priority is to encourage the private sector to work with us, sharing the risks and rewards of the regeneration process.

The purpose of this paper is to set out how English Partnerships has gone about its land reclamation work, to identify some of the barriers to achieving private investment in remediating contaminated sites, and to offer some suggestions as to how those barriers could be overcome.

The size of the problem, the size of the opportunity

To understand the economic potential of contaminated land, we need to know where it is and what its current use might be. Unfortunately, we have chosen not to survey contaminated land in such an exact manner, fearing the consequences of blight. We therefore need a proxy, and our best proxy is derelict land. It is not a great proxy. Less than 50% of derelict land is contaminated. And there is plenty of land that is contaminated but is not derelict. Nevertheless, it is a proxy that reveals quite a lot about where the problems and opportunities lie.

Unfortunately, we face another restriction. The national mapping exercise is very expensive. The last derelict land survey was carried in 1993. The next one is due this year but there are few signs that it will take place. It was for this reason that last year, English Partnerships and Ove Arup & Partners joined forces to predict the patterns of dereliction and, hence, contamination, over the next 10-15 years in England. We wanted to know what and where.

The starting point was the 1993 survey which found that just under 40,000 hectares of land was derelict, 35,000 hectares of which justified reclamation. Over a twenty year period, from 1974, the stock of derelict land had declined by 10%, but there had been a severe slowing up between 1988 and 1993 with a net reduction of just 2%.

Over that twenty year period we could clearly trace the following trends.

- a steady decline in the extent of spoil heaps, excavations and pits
- a recent increase in the amount of derelict land previously in military use, following cut backs in Defence budgets
- a progressive reduction in derelict land associated with railway land
- a marked increase in other forms of dereliction, including general industrial dereliction

By 1993, general industrial dereliction was by far the most extensive form of dereliction, totalling almost 47% of all recorded derelict land, as the UK emerged from 20 years of economic restructuring and a recent recession.

So what has been happening after that date. Our study concluded that new dereliction had probably been occurring at about the same rate as the previous period, about 1,700 hectares per annum. With English Partnerships funding the reclamation of about 1,000 hectares per year for the last 3 years, this action, when combined with the reclamation

work of other organisations, leads us to think that, in England, we are probably running to stand still.

What about the future? Overall, we are predicting that new dereliction will continue to be created at the rate about 1,500 hectares per year. Of this, we work on the assumption that English Partnerships will be called on to deal with about 40% of that total. We therefore need to reclaim about 600-650 hectares a year just to stand still. If we wanted to adopt a more ambitious agenda, at a reclamation rate of about 1,600 hectares a year, we might eradicate the stock of derelict land in about 35 years. This may give you some idea of the size of the task at hand.

But this is not the full picture. The age of regionalism is upon us. A partially devolved Scotland, an assembled Wales and Regional Development Agencies we need a regional dimension. We project that over the next few years, the northern regions will contribute the vast majority of new derelict and contaminated land, particularly the north west of the country. The south west has spewed up most of the historical dereliction that it is going to. The south eastern regions caused some distortion in the normal trends in the 1980s with the closure of the Kent mines, the recession and defence restructuring, but that distortion in the historical pattern is now beginning to settle down.

The role of English Partnerships

English Partnerships was established under the terms of the Leasehold Reform, Housing and Urban Development Act 1993 to promote the regeneration of areas of need through the reclamation, development or redevelopment of lands and buildings. In his statutory guidance to the new Agency, the Secretary of State for the Environment instructed English Partnerships to ensure that its programmes addressed the need for land for a variety of purposes, including industry and commerce, infrastructure, housing, leisure, recreation and green space, as well as the need to attract inward investment. The guidance further stated that English Partnerships' preferred mode of operations should be to act wherever possible as an enabling body, working in particular through the private sector.

The first task for the new Agency was to take its inheritance - English Estates, Derelict Land Grant and City Grant - and to create a new investment framework that reflected its statutory objectives and an operating culture that built upon its statutory guidance. One of English Partnerships' immediate priorities was to move away from the rigid demarcations between the previous funding regimes and we therefore created a unified and flexible Investment Fund to cover all forms of investment activity. Within the Investment Fund we have identified three separate programmes, primarily for management and accounting purposes. They are the Partnership Investment Programme which covers all our investments made by way of joint ventures and development agreements with third parties, particularly the private and voluntary sectors. The Programme represents our preferred method of working and will continue to expand. The second programme is our Land Reclamation Programme which includes the inherited derelict land grant schemes and also new local authority land reclamation projects. As we are able to involve other parties in

the reclamation and redevelopment process, a number of DLG-types schemes are moving into the Partnership Investment Programme. Finally, our Direct Development Programme is able to secure the provision of serviced land and industrial/commercial premises where there is an urgent requirement but we are unable to find development partners.

It is within this programme context, with its accent on flexibility, that English Partnerships considers its responsibilities towards the reclamation of derelict and contaminated land. In all our activities we are driven by the three objectives of engendering economic growth, creating employment and providing environmental improvements. Projects involving land reclamation are judged according to their proposed contribution towards the achievement of those objectives. The priority outputs by which project proposals are assessed reflect the objectives by measuring the jobs that a project will create and safeguard, the development that will achieved in terms of floorspace for various hard end uses, the quantity of housing that will be provided and the amount of land that will be reclaimed.

We are also driven by the need to maximise the value for money we receive from our investments. By involving the private sector at every opportunity and by levering in investment from other funding sources such as the European Regional Development Fund, we can finance more schemes and therefore increase our outputs. In 1997/98, our fourth full year of operation, we managed a development budget of £290M to produce a total investment of over £700M in regeneration activities.

In building a national reclamation strategy English Partnerships does not enter into a game of numbers. We are not charged by Government to reduce the quantity of derelict land by a given amount. Such a charge could actually distort priorities as the total level of dereliction is influenced by many factors of which English Partnerships' investment strategy is only one. Clearly, it is the Agency's interests to ensure that steady progress is maintained in bringing derelict sites back into use because there is a fundamental link to the national regeneration process. But of far greater importance to the Agency is its ability to prioritise at a project level by considering the total effect of its investment on a particular locality. Thus, the Agency may invest heavily in servicing a vacant but non-derelict site that has the potential to attract inward investment while deferring on an investment in a neighbouring derelict site that has little economic potential. Alternatively, the Agency may invest significant resources in a small inner-city area of extreme dereliction that will generate an output of only a few hectares of reclaimed land, but which will critically allow for the redevelopment of that area resulting in new jobs for local people. The Investment Fund gives English Partnerships and our partners the freedom to make such choices.

The barriers to private investment

While it is fair to say the public sector has a responsibility to lead the way, it cannot be expected to meet the challenge alone. To make any long-term impact we need to

understand why the private sector has so far been reluctant to invest in brownfield site development.

The barriers to significant private investment can be divided into three types - locational, legal and financial.

Land availability continues to be a constraint to investment -- the perception persists that the number of available brownfield sites will reduce over the next twenty years. The Ove Arup report shows that the figures simply do not bear this out.

There has also been a lack of knowledge on where the large strategic sites are located. And often once land has been identified, it is in multiple ownership, with poor access and servicing. In these circumstances, it is the role of the public sector to use its statutory powers and limited resources to assemble sites and make them attractive to developers.

A fundamental barrier to private sector investment is the neighbourhoods in which many of the potential sites are situate. Private developers are concerned with many factors, which usually revolve around uncertainties about the ability of the developments to hold their value over time.

There remains much confusion surrounding the impact of the polluter pay principle on the reclamation and development of brownfield sites. The inescapable fact is that, for as long as one remains the owner of a site, the possibility of statutory enforcement will remain.

The recurring theme in all of this is the perception of risk. The private sector can manage the cost equation provided they know what the majority of the figures in that equation are and will remain.

There is a lack of understanding about the track record of regeneration projects generally including mixed use developments. As a result the levels of risk and indeed the amounts of investments sought are perceived to be too high.

More generally, it is widely felt that the legal. financial and bureaucratic minefield which is thought to surround these developments makes the entire venture far too complicated and just too much of a hassle to get involved in. To be fair, it may also be true to say that a number of PFI ventures have struggled due to the lack of commercial understanding in Government Departments and Agencies.

But perhaps the single most effective barrier to private sector investment is the desire for a short term return on investment and this is something that can only be tackled through a change in attitude on behalf of investors.

Overcoming these barriers

There are a variety of financial and fiscal measures which the UK Government could consider to alter the balance of opportunity cost between greenfield and brownfield sites. A number of those suggested below were put forward by the UK Brownfield Group earlier this year, on which English Partnerships was represented.

Intervention in the form of project funding will continue to be critical in reducing uncertainty, particularly where locational advantage does *not* exist, rendering certain sites intrinsically *less* valuable than greenfield options. In such cases public funds should guide private investment. Traditional forms of public sector financial intervention – grants, gap funding and loans – need to be applied imaginatively and in a timely way. To some extent, these forms of intervention are becoming increasingly constrained as the European Commission tightens its state aid regime. This accentuates the need for the public sector to maximise best value for money for its investment. The main ways of achieving this are:

- involving the private sector as early as possible in the redevelopment process, so that the cost/value cap can be calculated across the entire project delivery process;
- maximising competition between private sector companies to test the market and drive down costs;
- ensuring the public sector shares in the value created through redevelopment, by use of equity stakes and clawback mechanisms.

There may also exists considerable potential for cross subsidisation of brownfield development with greenfield development. All options, including the introduction of a greenfield development tax need to be openly evaluated and proposals developed. If, however, a greenfield tax is introduced, it should be on a hypothecated basis with the receipts channelled directly into brownfield development and regeneration.

The potential of the Private Finance Initiative and other Public Private Partnership options also need to be properly explored. One possible option would be to attract private sector companies to promote or co-promote brownfield development schemes by procuring infrastructure requirements from them by way of a PFI deal. On complex schemes, this would give the private sector partner a steady income stream to tide them over until development receipts start to be generated on a significant scale. This would reduce the opportunity cost of complex mixed development schemes.

The public sector has also experimented over the last few years with the use of guarantees, particularly rental guarantees, in incentivising private sector development in difficult market locations. Rental guarantees, (set at say 80% of open market value)

can be potent and cost effective catalysts of regeneration.

Although the UK Enterprise Zones have proven expensive, and sometimes the benefits have not gone to those whom they were intended, i.e. the relocating companies, it may be that in extreme cases of prolonged market failure, some form of zoning mechanism may be appropriate. The types of area that might benefit are the coalfield areas and extreme peripheral areas such as Cornwall and West Cumbria. To prevent the leakage of Zone benefits, it may be that the designation of such areas should be restricted to land which is in public ownership.

It is also imperative that Government does not accidentally create financial disincentives to the prioritisation of brownfield sites. This almost happened last year when the regeneration agencies had to fight very hard for the introduction of an exemption from the landfill tax for the reclamation of contaminated land. In the absence of more innovative remediation technologies available on a commercial basis, it is imperative that this exemption remains in place for the foreseeable period, particularly if tax rates are going to rise.

Of course, the onus does not lie only with Government. Risk can also be managed through the provision of suitable insurance cover. The UK insurance market for remediated sites is currently very weak, with only a handful of providers. Over time, one would hope that more insurance companies will feel confident enough to move into this sector.

Policy into practice

(a) The coalfields

The policy is one thing but how do public/private sector partnerships work in the real world. English Partnerships role in the regeneration of the legacy of former the coal industry provides a graphic example of how well the relationship can work.

The regeneration of former coalfield sites is one of English Partnerships main priority areas. Over the next two year coalfield reclamation work is expected to account for 20% of the Agency's national budget. In November 1996, the Agency acquired a portfolio of 56 sites comprising over 2,200 hectares of highly contaminated land. The Agency has developed a 10 programme of reclamation for the portfolio expected to included a total public sector investment of up to £347 million.

To date over £20 million has been spent on the completing site surveys on each of the 56 sites and actual reclamation works have commenced on nearly a quarter of all sites.

Independent consultants have projected that the programme will create up to 52,000 jobs, develop over 4,000 new homes and attract over £750 million of private sector investment.

(b) Greenwich peninsula

English Partnerships is also involved in the reclamation and servicing of the Greenwich Peninsula. The 118 hectare site forms part of the Agency's long-term strategy for the regeneration of the Thames Gateway and in the short-term will be used as part of the Millennium Exhibition.

The highly contaminated former gas works site was purchased in February 1997 from British Gas Properties to ensure that the entire Peninsula could be regenerated to a high standard. To date the Agency has spent over £70 million on the site.

Central to the development of the site is a mixed use development incorporating up to 3,000 homes, a primary school, health centre, restaurants, a hotel, cinema, parks and a riverside walkway.

It is expected the development will create over 5,300 new jobs and with receipts from land sales and private sector investment, provide a favourable return on public sector investment.

What must happen next?

The essential fabric of our urban landscape is the tightly woven fabric of the past - the areas of our country where industry once stood but has long gone, whilst the communities that served those industries remain. Brownfield sites are the legacy - derelict, contaminated, vacant or underused. And it is to those sites that our commitment and our investment as public funding providers must be directed, however difficult the terrain.

We have made tremendous progress at English Partnerships in the last three years. We are now hopeful that the state will provide the policy framework required and by pooling resources the public sector can make its contribution. The private sector must now take up the brownfield challenge - private investors must take on more of the risk. Not out of a sense of public spirit or because it is the right thing to do but for the simple reason that there is money to be made in regenerating contaminated land.

The Redevelopment of Contaminated Land for Housing Use

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Key words: contaminated sites, housing, legislation, values, real estate

The present lack of legislation dealing specifically with land contamination is creating problems for real estate professionals practising in the United Kingdom. Housing developers and their advisors have to use their best judgement in deciding whether or not development sites are likely to fall within an official definition of 'contaminated land' and to plan soil treatment accordingly. Recent research has shown that potential uyers and renters of new housing are prepared to live on former contaminated sites but they expect to be informed about former land uses and remediation work which has been undertaken. Housebuilders, on the other hand, are often reluctant to provide this information through fear that it may be commercially damaging. There is considerable variation in the approach adopted by local planning authorities when considering applications for housing development on contaminated sites and there are marked differences in the knowledge of real estate professionals.

Contaminated Soil '98, Thomas Telford, London, 1998, 671–679

Introduction - 'brownfields' and land contamination

The term 'brownfield' is widely used in both the United States and the United Kingdom, as well as other industrialised nations, but no uniformly agreed definition exists for the term. When considering the re-use of 'brownfield' land it is essential to have a clear understanding as to what is meant by the term in the context in which it is used. One definition used in the United States is:

> '***brownfield:*** *abandoned, idled or underused industrial and commercial facility where expansion or redevelopment is complicated by real or perceived environmental contamination.'* (Fields, 1995)

This definition provides a clear link between brownfield land and contamination, regardless of whether such contamination physically exists, whereas the linkage is not so positive in the general usage of the term in the United Kingdom, as evidenced by the following definition:

> '***brownfield:*** ..... *any areas of land which have previously been the subject of a man-made or non-agricultural use of any type. This would include industrial uses such as chemical works, heavy engineering, shipbuilding and textile processing, together with unfit housing clearance sites and docklands ..... as well as mineral extraction sites and those used for landfill purposes.'* (Syms, 1994)

The difference in approach between the two countries may be due, at least in part, to the fact that there is a limited supply of development land in the UK and the heavily industrialised nature of some parts of the country. These two factors have resulted in a need to re-use land. Until relatively recently, contamination was not perceived by the real estate profession as being a major issue. Contaminated sites had been dealt with as part of the process of preparing land for redevelopment and was regarded by real estate surveyors and valuers as being more of an issue for their colleagues in engineering and environmental sciences.

This state of affairs existed until about May 1991 when real estate practioners generally came to appreciate the relevance of the Environmental Protection Act 1990, which came into effect in January 1991. A consultation document in respect of the proposed registers of potentially contaminative land uses (Department of the Environment, 1991) produced an outcry from even responsible professional associations and trade organisations. The main reason was that, by identifing some activities as having the potential to cause contamination, the values of properties used for those purposes would be severely blighted, perhaps even to the extent that they would become unsaleable. In the face of continued opposition, the proposed registers were abandoned two years later but, due to increased concern about environmental standards, land contamination has achieved a higher profile, particularly amongst those directly engaged in the development process.

What is contaminated land? - the legal definition in the United Kingdom

Man made contamination originates from industrial processes, current or historic, and activities such as landfilling, as well as from environmental accidents. In countries such as the United Kingdom, with a long history of industrial land use, contamination and its treatment will inevitably be an important factor in bringing disused or derelict land back into use. Legislation proposals in the United Kingdom have focused on man made contamination and, for this reason, this paper does not include problems relating to naturally occurring contamination.

Many different definitions of 'contaminated land' have been considered over the course of the last ten years and the emphasis changes according to the viewpoint of the individual or organisation proposing the definition. These definitions are discussed in Syms (1997a) but, in practice, the general approach seems to imply that the terms 'contamination' and 'pollution' are more or less synonymous and they are often used interchangeably.

A legal definition of 'contaminated land' was introduced to the United Kingdom for the first time, in section 57 of the Environment Act 1995, which defined contaminated land as being:

> **any land which appears to the local authority in whose area it is situated to be in such a condition, by reason of substances in, on or under the land, that -**
> **a) significant harm is being caused or there is a significant possibility of such harm being caused; or**
> **(b) pollution of controlled waters is being, or is likely to be, caused;**

'Harm' is defined in the 1995 Act as meaning "harm to the health of living organisms or other interference with the ecological systems of which they form part". In the human context, this is intended to include harm to property. The word 'significant' is not defined in the Act and its use as part of the definition of contaminated land narrows the scope of the legal meaning of the term.

In September 1996, following public consultation, the Department of the Environment published its proposed definition of 'significant harm' (Department of the Environment, 1996). This identified four categories of receptors, or targets, which may suffer 'significant harm' for contaminated sites, these are:

- human beings, who suffer death, serious injury, cancer or other disease, including genetic mutation or the impairment of reproductive functions;
- living organisms or ecological systems, but only those which are endangered and/or protected by UK or European legislation;
- livestock and crops, including fishing and shooting rights, which suffer a significant loss of production or value;
- buildings which suffer structural failure or substantial damage which renders them unsuitable for their intended use.

The House of Commons Select Committee on the Environment subsequently considered the Department's proposed definition in the context of the 1995 Act and expressed concern over the narrowness of the definition, as well as the burden being placed on local authorities (House of Commons, 1996). The Royal Institution of Chartered Surveyors in evidence to the Select Committee criticised the consultation draft for its lack of 'plain English' (RICS, 1996).

Implementation of the legislation was delayed due to the general Election on 1st May 1997 and since then the present government has been considering its options. A final conclusion has yet to be reached in respect of a legal definition of contaminated land. There is no doubt, however, that the DETR's intention has been to define 'contaminated land' in a narrow sense, so as to focus on the most severely contaminated sites. This approach is regarded with concern by some environmental groups but may be considered appropriate by others, in terms of the allocation of resources and limiting the blighting effect on property values.

From the viewpoint of housing developers engaged in the re-use of 'brownfield' land the continuing lack of effective legislation is simply prolonging a state of uncertainty which has existed since the first consultation paper on land use registers was published in 1991. Developers therefore have to make a judgement as to whether or not the site of a proposed development would fall within the legal definition. This is important to house builders who plan their production programmes two or more years in advance, as it will affect their decision making processes both as to whether or not to acquire sites for their land banks and as to the remediation methods to be employed.

Housing development on land affected by contaminative substances

The Department of the Environment's Green Paper *'Household Growth: where shall we live'* states that according to the latest set of household projections, published in 1995, "there could be up to 4.4 million more households in England between 1991 and 2016" (Department of the Environment, 1996, p1). If this projected growth is proved to be correct, and the observation is made in the Green Paper that actual growth in the number of households has been understated by earlier projections, considerable pressures will come to bear in order to ensure that an adequate supply of residential development land is made available. The same report goes on to suggest that "an aspirational target of 60%" be set for the re-use of previously used, or 'brownfield' land, and asks whether or not an even higher target for re-use could be achieved.

The anticipated growth in household numbers is not due to a projected increase in population but more to changes in the structure of households. Almost 80% (3.5 million) of the total projected growth to 2016 occurs in **one person households**. (Department of the Environment, 1996, p7) Three main sources are identified for the growth in single person households, over half as a result of single, never married, people living on their own, a third through divorce or separation and the

remainder due to widowhood. Household growth requirements vary significantly from region to region, ranging from an increase of 13% in Merseyside to 29% in both the South West and Eastern regions. One of the most important reasons for the regional variation is migration between regions, including some international migration.

In some parts of the country, notably London and Merseyside, the percentage of new residential development taking place on previously used land already exceeds the Green Paper's 'aspirational' target of 60%. In London re-used land accounted for 83% of all land developed for housing in 1993 and in Merseyside the equivalent figure was 76%. By contrast, the re-use of land for housing purposes represented only 32% and 33% respectively of all residential development in the East Midlands and the South West regions. In many of the major cities the easier redevelopment options have already been taken up, leaving behind sites with severe problems, whilst in more rural areas there still remains an adequate choice of 'greenfield' sites which will tend to be redeveloped in preference to brownfields. The mismatch between available brownfield land, which is capable of redevelopment, and housing demand is seen as the major obstacle in achieving the target set out in the Green Paper.

The extent to which the sentiments of the Green Paper are supported by the present government is somewhat unclear. In the latter part of 1997 the indications were that Government considered the 'brownfield' redevelopment targets to be unrealistic and that more greenfield land would have to be released in order to meet housing demand (Nuttall and Kelly, 1997). This produced an outcry from environmentalists, resulting in a statement that the Government wanted to see as many households as possible accommodated in areas that have already been developed (Prescott, 1998).

Perceptions of risk in the redevelopment of contaminated land for housing

Recent research supported by the Joseph Rowntree Foundation (Syms, 1997b) has sought to identify the major issues, in terms of risk perception, which surround the redevelopment of contaminated land for housing use.

Addressing the need to re-use brownfield land, contaminated as a result of past industrial activities, the research sought to examine three issues. First, whether members of the public were prepared to live in houses built on land which had been affected by contamination. Second was the degree of reassurance which those same individuals may require, if indeed they wish to be informed, with regard to the contamination risks. Third was the interaction between the various actors in the redevelopment process, both in the public and private sectors. Do these actors work well together or is there room for improvement in relationships?

In answering these questions mechanisms for communicating information about contaminated land need to be considered.

The principal conclusions from the research were as follows:

- the general public regards contaminated land as being somewhere in the mid-range of every day environmental hazards and would wish to be informed about contamination issues on development sites.

- private house builders generally are reluctant to divulge information about projects on former contaminated sites - either for research purposes or to purchasers.

- housing associations generally have been more willing to develop on contaminated land than private house builders but, as a rule, even they do not make information available to their tenants.

- the approach adopted by planning authorities is extremely variable and confusion exists as to the relative responsibilities of the different departments, within authorities, and the Environment Agency, tending to cause frustration amongst intending developers.

- There was a widespread belief amongst the general public, financial institutions, developers and estate agents that government should take the lead in securing the re-use of contaminated land.

- of the funding institutions, traditional banks are more aware of the issues, and have appropriate mechanisms in place, than the building societies, or former societies which have converted to banks; none of the mechanisms discriminated against the redevelopment of contaminated land.

- residential estate agents and the valuers of residential property have a poorly developed knowledge concerning contaminated land, even when they have been involved in its acquisition, disposal or redevelopment.

- the time taken by English Partnerships to process grant applications is a source of frustration for developers and many housing associations would also like to see the grant process streamlined between English Partnerships and the Housing Corporation.

Preparing land for housing development

The issues identified in the research report should be taken into account when considering whether or not a previously used site is suitable for residential development. As demonstrated by the Green Paper, previously used sites are being

redeveloped, however, not all land affected by contamination is suitable for housing development. It may be in the wrong location, or the past uses on the land may be such as to prove an insurmountable hurdle, in terms of either remediation cost or risk perception.

Developers need to decide whether or not they wish to become involved with the redevelopment of previously used land, especially land affected by contamination. The research found that many house builders see the risks as being too great, or they operate in parts of the country where there is still an adequate supply of greenfield land, so there is less pressure on them to re-use land. On the other hand, a considerable number of developers have been very successful in redeveloping brownfield land. Although some exceptions were found, these tended to be the larger house builders, with several major companies having established specialist divisions to undertake brownfield redevelopment.

If developers are to embark upon the redevelopment of brownfield sites, which may be affected by contamination if not actually designated as contaminated land, then they and their professional advisors need to gain the best understanding possible of the land in question. First and foremost comes the site investigation. This involves far more than simply digging a few holes, as many developers have found to their cost.

The research discovered a considerable variation in approach between housing developers when it came to site investigations. Some developers would not enter into a binding commitment to acquire sites until such time as they had completed thorough geo-technical and environmental surveys, whereas others completed their purchases having obtained only a minimal amount of historical information about the site. Predominant in the latter group were housing associations, providing social housing in inner city locations, some of whom felt that it was incumbant on them to take greater risks in order to provide homes where they were most needed.

Assuming that contaminants are found in the land, then the selection of site remediation methods needs to be undertaken. The study found that the two most popular methods used by housing developers in the UK are:

- total excavation of the contaminated material and its disposal to licensed landfill, often associated with the import of clean fill material; and
- the construction of an impermeable cover layer, so as to contain the contamination on site.

A variation on these is partial excavation and removal of contaminated 'hot-spots', with the on-site containment of contaminated residues. House builders tend to be rather wary of employing what may be perceived as 'high-tech' methods, such as bio-remediation and chemical treatments, as they are concerned about public acceptability.

Market Acceptance

Regardless of the method of remediation selected to prepare the site for development, the most important matter is to ensure that the treated site will achieve acceptability in the market place. The research supported by the Joseph Rowntree Foundation included psychometric studies of professionals involved in the redevelopment, funding and sales of housing constructed on former contaminated sites, together with members of the general public, potential buyers or renters of such homes. The study attempted to assess the perceptions of known and unknown risks, or uncertainties, associated with contaminated land, when considered in context with a number of other, everyday, environmental hazards. For most people the known risks were somewhere in the mid-range of risk perceptions but the unknown risks were perceived as being much higher on the scale. There was also widespread agreement that the perceived greatest threat from land contamination was potential harm to drinking water.

Another important issue raised by the research was that, whilst house buyers and renters wish to be informed about historic land uses and soil treatments, the information provided by developers is extremely variable. Some developers profess to make information available, whereas in reality they provide very little, whilst others consider that to supply information would be detrimental to their businesses. In the majority of cases it would seem that it is left to solicitors to obtain the relevant information but not all solicitors are diligent in this respect.

For many people therefore, the first they may know about the past uses of land on which their new home is built, or about any contamination, is when they come to hear about it from local residents. The concerns of the house builders and the ways in which information may be communicated to the house buying and renting public, in a non-frightening manner, are being considered by the house building trade associations and other bodies.

Conclusion

Land which has been contaminated by past industrial uses can be successfully reclaimed for residential development. Such redevelopment should not be regarded as being solely for low-cost or 'social' housing, although many developments are aimed at these markets due to the inner city location of many contaminated sites. It should be stressed that, so far as public risk perceptions are concerned, by no means all land which may eventually be legally designated as 'contaminated' will be suitable for residential use. It may therefore be the case that residential developments are more likely to take place within the 'grey area' of land affected by contaminative substances, thus falling outside the legal definition.

Research has found that the general public does not consider the re-use of land for housing to be unacceptable and regards the risks involved as being in the mid-range

of those associated with everyday hazards, although there is a greater fear of the unknown. People expect to be informed about former land uses and remediation work which has been undertaken and to receive appropriate guarantees to ensure that, if any problems arise in the future, the builder will put it right. Concealment of information by builders, in the belief that it may be commercially damaging, will only lead to greater suspicion when the facts become known.

Site investigations, including comprehensive historical studies, are required in order to assess the suitability of land for residential development. Accurate record keeping on site and the preparation of a post-completion report are also essential. It is not suggested that 'health warnings' form part of sales particulars but it may be appropriate to show 'before and after' photographs in sales offices.

Effective legislation in respect of contaminated land, both in 'cleaning up' the past and preventing further contamination, is long overdue. It is to be hoped that this will be brought into effect in the near future. The real estate professions, housing developers, engineers, lawyers and the regulators will all have to work together in ensuring that this land is brought back into use.

Copies of the full report *The Redevelopment of Contaminated Land for Housing Use* can be obtained from the ISVA, 3 Cadogan Gate, London, SW1X 0AS. Tel: 0171 235 2282, fax: 0171 235 4390. Price £9-95 plus £2-50 post and packing.

A training video based on the research report, including a detailed case study, has been produced by the Chartered Surveyors Education Channel. Further details are available from Television Education Network Limited, 15 Jockey's Fields, London, WC1R 4BW. Tel 0500 826764 Fax 0171 753 8761

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REMEDIATION IN THE LUSATIA AND THE CENTRAL-GERMAN LIGNITE MINING AREAS

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Key words: miming, environmental impact, environmental policy instruments, national programmes, abandoned waste disposal sites, contaminated sites, groundwater monitoring, remediation,

SUMMARY

Lignite mining is one of the chief tasks resulting from German unification. Starting from a description of the consequences of intensive lignite mining and the resulting environmental impacts, an outline if given of the scope of this task, of the main issues it involves and of the approaches used to tackle it. In addition to legal and financial aspects, the contribution deals with technical aspects of contaminated sites remediation and with the necessary cooperation between the Federation and the federal states (Länder).

KURZFASSUNG

Die Braunkohlesanierung ist eine der Schwerpunktaufgaben bei der Realisierung der deutschen Einheit. Ausgehend von der Beschreibung der Folgen des intensiven Braunkohleabbaus und der daraus resultierenden Umwelteinflüsse werden Umfang, thematische Schwerpunkte und Lösungswege für die Umsetzung dieser Aufgabe skizziert. Neben den rechtlichen und finanziellen Rahmenbedingungen werden fachliche Aspekte für die Altlastensanierung und die dazu erforderliche Zusammenarbeit von Bund und Ländern dargestellt.

Contaminated Soil '98, Thomas Telford, London, 1998, 681–690

1. INTRODUCTION

Lignite mining on the territory of the former GDR was concentrated on two areas. The Lusatia area is located in the south-east, in Brandenburg and Saxony. The area in Central Germany covers areas parts of Saxony-Anhalt, Saxony and Thuringia.

The lignite mining tradition in both areas dates back to the previous century and it was a main source of the industrial and infrastructural development of these areas. In the 1980s roughly 310 megatons lignite were produced annually. Some 200 megatons of crude brown coal per year were used in thermal power stations and heating stations. Over 100 megatons were briquetted. They were used as domestic and industrial fuels, in thermal processes, gasification and degasification, and in the chemical industry.

In terms of its environmental impact, lignite mining's legacy is particularly evident in three sectors: In addition to the devastation of landscapes and the natural environment, this impact includes in particular long-term changes to the groundwater system as well as hazards emanating from former industrial and waste disposal sites. The effects of these impact categories combined is what makes remediation in the field of lignite mining such a particular challenge. According to the then-existing Lignite Mining Remediation Office[i], the remediation task for the Lusatian and Central German mining areas extends to 159 opencast mines shut down or worked out, 178 km of slopes requiring safety measures, 3097 ha of dump sites and 38 upgrading facilities.

1029 sites suspected of being contaminated, both former industrial and waste disposal sites, characterize the fall of this sector of industry in the territory of the new German federal Länder (federal states).

Among the vastest environmental damage is the disturbance of the water balance of entire regions. In terms of static supplies and the volume of water required to fill up worked-out opencast mines, the groundwater deficit in the Lusatian mining area alone is assumed to come to 13 billion m^3. Moreover, this area is low in precipitation, with very low groundwater recharge rates. Adding to the problem is that entire ecosystems have adapted to the elevated discharge of receiving waters that existed over decades as a result of the mining activities. Areas affected by this include e.g. the Spreewald, a unique nature reserve, or the lakes supplying Berlin with drinking water. The envisaged additional use of surface water to flood opencast worked-out mines further aggravates the situation.

2. REMEDIATION APPROACHES

2.1 UNDERLYING LEGISLATION AND STRUCTURE

Article 55 of the Federal Mining Act[ii] requires the mine owner to draw up a final operation plan for the purpose of making the land used by him within the framework of his entrepreneurial activities fit for subsequent use while safeguarding public safety and

ensuring the usability of the land. This includes in particular the elimination of impending hazards, the cleanup of contaminated land as well as measures to ensure that no risks emanate from land formerly used. Furthermore, agreement must be reached with the authorities representing public concerns with respect to the usability. Only when these prerequisites have been met by the mine owner can he be released from supervision by the competent mining authority and, hence, responsibility be transferred to the subsequent user.

In connection with German unification, ownership of the mines passed into the hands of the Treuhand privatization agency, which explains the financial responsibility of the Federal Government for the remediation of the lignite mines. The Administrative Agreement of 1 December 1992 between the Federal Republic of Germany and the Länder Berlin, Brandenburg, Mecklenburg-Western Pomerania, Saxony Anhalt, Thuringia and the Free State of Saxony on the financing of contaminated sites remediation[iii] created the financial basis for the rehabilitation of major industries and the lignite mining sector. Under this administrative agreement, remediation in the lignite mining sector alone is receiving funds amounting to DM 1.5 billion annually over a period provisionally limited to the end of 1997. A subsequent agreement extending to the year 2002 has now been concluded, which provides for an annual budget of approx. DM 1.2 billion. The new feature under this agreement is that, over and beyond measures to meet existing obligation under mining law, it introduces the possibility to finance measures aimed at improving the water balance and the infrastructure in the regions to be rehabilitated. For such projects, however, the Länder's contribution to the financing is higher than the 25% they are otherwise required to contribute.

For all mines still governed by mining law a company was founded as the legal successor. This company, which also manages lignite mining remediation, now called the „Lausitzer und Mitteldeutsche Bergbau-Verwaltungsgesellschaft mbH" (LMBV for short), is wholly owned by the Federation. Since the above-mentioned administrative agreement included a financing commitment on the part of both the Federal Government and the Länder, there was the need to create instruments which ensure that in tackling the task common agreement is maintained and justified interests are safeguarded.

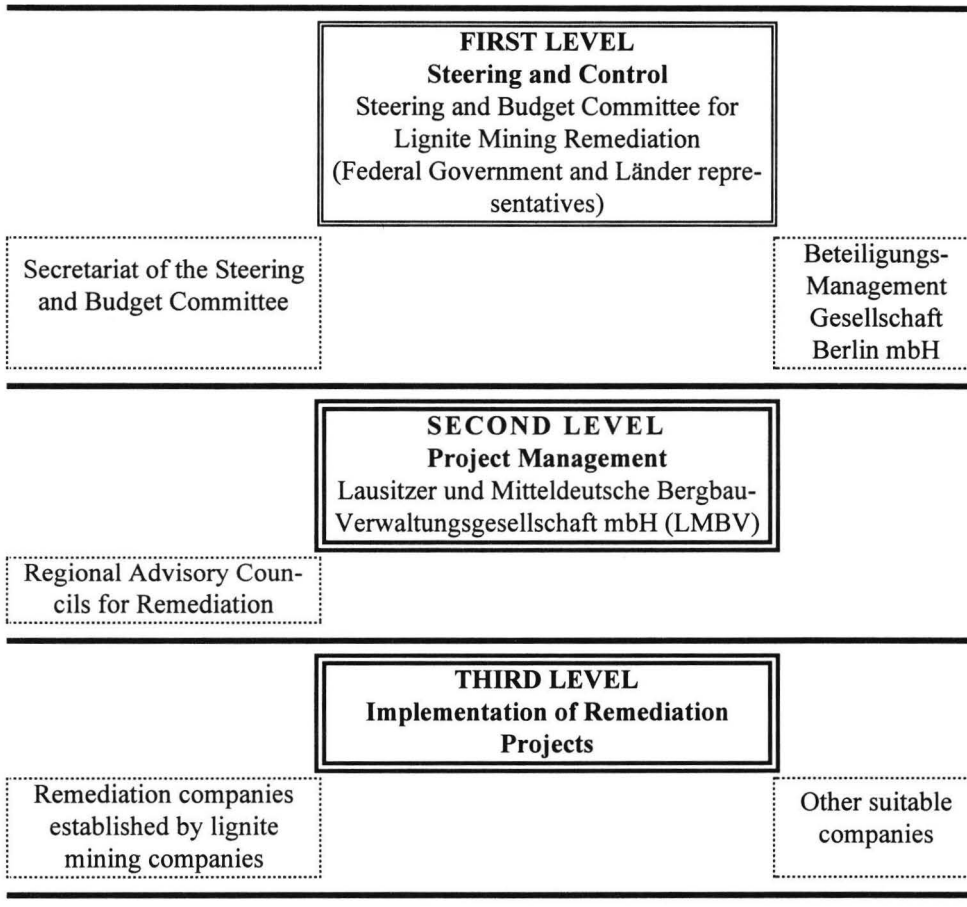

Figure 1: Structure of lignite mining rehabilitation since 1997 [after [iii]]

2.2 NATURE AND VOLUME OF THE TASK

Lignite mining remediation is a collective term comprising a variety of measures imposed on mining companies by the Federal Mining Act in order to ensure that no risks emanate from land formerly used for mining purposes. The various tasks are closely interlinked in some cases, necessitating complex, supraregional solutions. An interdisciplinary and harmonized approach must therefore be pursued in tackling them. In performing measures, the focus initially was on work to dismantle facilities as well as on earth moving works aimed at restoring geotechnical safety. These measures, which although sometimes simple are resource- and labour-intensive, have largely been completed. At present we are seeing an increase in measures which can only be carried out by specialized firms.

Remediation of lignite mining areas					
Geomechanical problems	Restoration		Groundwater management	Landscape planning and ecological aspects	Contaminated sites
Handling of the problem of the deficiency of overburden	Reclamation		Water demand for filling opencast mines (water quantity)	Concept for reuse of the former mining areas	Abandoned industrial sites near or in opencast mines
Design and safety measures at slopes and dumps	Stage 1: technical recultivation Stage 2: biological recultivation		Water quality problems	Drafting of ecological requirements	Abandoned industrial sites (refining facilities)
Design and use of worked-out mines	Agricultural reuse	Reuse as forest area	Use of water from rivers to refill opencast mines	Certificate of discharge for the responsibility of mining areas from the mining authority	Abandoned waste disposal sites with material from the mining process
Geomechancial problems with uniform grain size in the overburden called „Setzungsfließen“	Utilisation of ash and sewage sludge for recultivation		Hydraulic engineering/ water-reservoir management	Planning and construction of biotops and wetlands	Abandoned waste disposal sites for the disposal of waste from other industries or of residential waste
Unstable „old“-underground mines				Identification and management of succession areas	Contaminated sites affected by groundwater lowering

Table 1: Main topics of remediation in lignite mining areas

A tendency to be observed as a result is that the desired job-creation effect has been impossible to maintain at previous levels. Often, there are time constraints which either require projects to be performed quickly or necessitate interim solutions in the form of an additional lowering of the groundwater table. There is a continual need here for micro-economic optimization in the sense of a minimization of costs.

The issues and dimensions outlined, and the expected cost of lignite mining remediation, necessitate corresponding planning and implementation. Those involved were sometimes faced with tasks for which no solution was available, the scientific fundamentals were not entirely clarified, no practical experience existed or whose implementation would have been extremely costly. This meant an enormous need for intelligent and goal-oriented technical solutions. The situation was also characterized to a certain extent by time constraints, brought on in particular by a rise of the groundwater table and the social relevance of the task.

The Umweltbundesamt itself is not directly involved in lignite mining remediation, since the federal structures of the Federal Republic of Germany allocate responsibility for this task to the Länder. Nevertheless, there are a number of technical issues which are in need of clarification and which influence the scope and cost of remedial work considerably. As a higher scientific federal authority, the involvement of the Umweltbundesamt in the investigation of these issues is based on the fact that the Federal Government bears 75% of the cost of remediation and thus has a substantial interest in seeing them clarified. As described earlier, lignite mining remediation has raised a multitude of technical questions for which solutions do not yet exist or cannot yet be considered as validated. The complexity of the research required would overtax the budget and go beyond the sphere of responsibility of a single department. That is why Federation/Länder working groups have been established to separately deal with the topics recultivation/ecology, general water management planning, and contaminated sites, whose task it is to coordinate the research work and to provide it with technical guidance.

By generating minimum requirements and working aids, the projects initiated are intended to decisively determine the course taken in contaminated site remediation. They are also intended to produce validated sets of data for use in the planning of demanding and complex remedial solutions.

2.3 CLEAN UP OF COTAMINATED SITES AS A SPECIAL ELEMENT OF THE MINING REMEDIATION PROGRAMME

Contaminated sites in the „classical" sense will be dealt with in more detail in the following, i.e. land whose topsoil and/or underlying soils are contaminated as a result of past activities, thereby endangering or posing a risk to human health, the environment or otherwise interfering with public safety. Contaminated sites comprise both former waste disposal and former industrial sites (also cf. [iv])

A suspicion of mining-related contamination can be assumed to be warranted in the case of the following sites:

- recultivated land to which mining-related waste was applied as soil improver;
- sedimentation plants for effluents from coal upgrading plants, flushing dumps
- opencast mining pits used in the past to deposit industrial and municipal wastes;
- coal upgrading plants and facilities;
- other installations of mining companies (workshops, rail haulage installations, storage areas and the like).

These sites have, on the one hand, characteristics comparable with those of conventional contaminated sites and, on the other hand, exhibit very special features typical of the mining sector. These include in particular the often markedly larger size of the sites in terms of both surface area and volume, their considerable depth, and large differences in the prevailing geological conditions.

An outline is given below of the particularities and special conditions applying in lignite mining remediation.

Complex assessments of the hazards emanating from former mining sites must take a multitude of factors into account, such as:

- structure of the deposits, makeup of layers, geological faults, properties of the overburden and of the resource;
- structure of groundwater horizons and their hydraulic connection, direction of groundwater flow;
- amount of water pumped and the size of the cone of depression;
- timeframe for remediation as results from a rise in the water table;
- site exploration status as regards the spectrum of pollutants present, the duration of contamination, the location, the quantities involved, and the reliability of the data;
- prognosis and current knowledge about geological processes, taking the groundwater's acidity into particular account; and
- existence or initiation of conditions for the activation of pollutant potentials or accelerating the release of contaminants.

The discontinuation or drastic reduction of lignite mining activities in the areas dealt with here has been accompanied by reduced water pumpage in the mines. As a result, the distances between groundwater and overlying contaminated land are becoming smaller. The rise of the groundwater table carries the risk of enhancing hazard potentials when the water comes into contact with contaminants present. What is necessary, therefore, is to undertake a comprehensive analysis and a comparison at the microeconomic level as to how the cleanup of contaminated sites and the rise in the water table can be monitored with a view to establishing a sound balance between required remediation work and financial resources available.

Sites which are of relevance in this context not only include the 1026 sites identified so far as suspected contaminated sites covered by mining law, but also those at which contaminant transfer had been limited by the mining-related lowering of the groundwater table to such an extent that they did not represent a hazard. These additional sites suspected of being of relevance are currently estimated to number about 4000 and include in particular former industrial sites, former municipal and industrial waste dumps, and not least of all former military sites and armaments-contaminated sites. Differences in competencies and ownership were further impediments to obtaining an overall picture of the actual hazard potential emanating from relevant sites in the regions affected by the lowering of the groundwater table. That is why the Umweltbundesamt has performed a project to investigate this issue.

Based on a geo-information system, data from geohydrological models depicting the temporal course of the renewed rise of the groundwater table over large areas were compared with data obtained in the investigation of suspected contaminated sites. Multitemporal analysis of the two sets of data allows the time of contact with groundwater to be determined within the limits of the data base's accuracy. This in turn allows sites for priority treatment to be identified. In other words, at the calculated time of contact with the rising groundwater the actual hazard potential of the site concerned must be known and any resulting remedial work must already have been completed. Since both sets of data are subject to continual change, interfaces have been created which permit the input data to be updated. The competent authorities are thus provided with a working tool in the form of a warning system which enables them to set priorities and to use the limited public funds available for contaminated sites exploration and remediation in an appropriate and case-specific manner. Guidance was provided to this project by a group of representatives of the Federal Government and the Länder. It is planned to periodically update the data base and modify the interfaces for use by the affected Länder for their contaminated sites registers.

3. INTERIM RESULTS OF THE LIGNITE MINING REMEDIATION PROGRAMME

In our view, the experience gained and priority tasks identified so far in lignite mining remediation can be summarized as follows:

Management

The organizational structure of lignite mining remediation as shown in figure 1 ensures an effective participation of both the Federal Government and the federal Länder as well as the inclusion of such aspects as subsequent use and planning at the Land level.

The administrative agreement and the financing provisions it contains can be regarded as having set lignite mining remediation on its course and through the Federation/Länder cost sharing arrangement ensures continued interest in shaping, implementing and optimizing the necessary remedial measures.

The broad participation of specialized authorities and regional administrative bodies furthers the reaching of a consensus on measures to be taken as well as goodwill towards the project manager LMBV.

The numerous possible forms of participation, however, also require a hierarchical structure, in order to ensure the continuation of the work.

Contaminated sites

Opencast lignite mining pits formerly used to dump waste from the chemical industry are particularly problematic since in addition to the nature of the waste dumped, factors adding to the cost also include the volume and thickness of the dump. If classical remediation techniques are used, the cost of cleanup can be expected to be enormous and nearly impossible to finance.

Thermal upgrading (coking, low-temperature carbonization) plants were found to involve a high risk potential. The risk potential of briquetting plant is lower, and of local influence only.

Certain site characteristics typical of the sites' respective former uses provide the opportunity to exploit synergy potentials which may allow site investigation to be optimized and use to be made of analogous remediation techniques. This nevertheless involves the need for site-specific examination and compliance with specific minimum requirements.

Choosing the appropriate contaminated site remediation technique requires a complex analysis of the site conditions, the overall water resources management concept (in both quantitative and qualitative terms) and the site's mining history as well as the availability of comprehensive information on the site.

The complexity of the sites involved necessitates the installation of long-term monitoring systems or elements which allow the effectiveness of remedial measures to be verified and sites not yet rehabilitated or contained to be monitored.

Tasks in the field of water resources management

The rise of the groundwater table resulting from reduced water pumpage can cause the hazard potential of contaminated sites to change significantly, as can geological processes. This has to be taken into account when selecting and timing remedial measures.

Protecting the groundwater and restoring the water regime to a condition where it is largely self-regulating are essential aims of the cleanup of sites contaminated as a result of mining activities.

Flooding with surface water appears to be the most effective means at present to counteract the impending risk of flooded pits acidifying as a result of a natural rise in the groundwater table. Even if this is done, however, appropriate management and aftercare of the water bodies so created remains indispensable.

4. OUTLOOK

The funding provided by the Federal Government and the Länder has made it possible for measures in the field of lignite mining remediation to be initiated relatively quickly and in a qualified manner. The review of the work done so far confirms that many of the measures necessary have already been implemented. Nevertheless, considerable residual work has yet to be done in the areas of contaminated sites remediation and rehabilitation of the water regime.

The objective of the mine operator is for the devastated and subsequently rehabilitated land to be released from supervision under mining law. The land's subsequent use plays no insignificant role in this context, since it determines the necessary extent of remedial work. That is why the mine owner will join the negotiations with the competent Land planning authorities and the regional administrative bodies at an early stage in order to obtain the required planning security. For former industrial sites, we are seeing equivalent subsequent uses which can be regarded as appropriate and reasonable. The allocation of land devastated as a result of mining activities requires binding decisions on regional use concepts to be made by the participating Land planning authorities. It is becoming clear in this context how much the rehabilitation of contaminated mining sites affects a wide variety of interests. Finding a consistent approach to tackling the task requires constructive interplay characterized by a high degree of trust, responsibility and cooperation. This is the only way in which a lasting structural change can be effected in mining regions. For the two mining areas in the eastern part of Germany, the programme to rehabilitate the lignite mining sector no doubt has provided the initial spark.

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THE REUSE OF A FORMER MGP SITE IN MILANO (ITALY)

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Key Words: industrial sites, reuse (of sites), legislation, environmental investigations, authorities' role, soil and groundwater contamination, limiting values and standard, costs, risk analysis, clean-up technologies.

SUMMARY
The site, about 430,000 m^2, has been utilized for about 80 years for the production of gas distributed in Milan. For the reuse of the site investigations have been carried out to verify the degree of soil and groundwater contamination (PAH, As, Pb). By comparing the results of investigation with the limiting values of contamination accepted by legislation, the arrangement of clean-up and containment interventions has proved necessary and it is now in the design stage. To define the maximum concentration values that are the aim of clean-up a risk analysis has been carried out.

KURZFASSUNG
Das im Betreff genannte Industriegebiet, ca. 430.000 m^2 ,wurde für ca. 80 Jahre zur Produktion von Gas verwendet. Für die Wiederbenutzung des Industriegebietes, in Übereinstimmung mit den Kontrollwesen und mit den zukünftigen Benutzern dieser Strukturen wurden Nachforschungen angestellt, damit die Verseuchung von Boden und Grundwasser festgestellt werden konnte (PAH, As, Pb). Bei einem Vergleich dieser Ergebnisse mit den gesetzlich vorgesehenen und zugelassenen Verseuchungsgrenzen zeigte sich die Notwendigkeit, Sicherheits- und Vergütungssarbeiten in diesem Gebiet vorzunehmen. Um die maximalen Verseuchungskonzentrationen, die Ziel dieser Vergütung sind, festzustellen wurde eine Risikenanalyse notwendig.

RÉSUME
L'installation industrielle, 430.000 m^2 environ, a été utilisée pour près de 80 ans pour la production du gaz distribué a Milan. Pour sa réutilisation on a mené des enquêtes afin de verifier le niveau de contamination du terrain et des eaux souterraines (PAH, As, Pb).De la comparaison entre le résultas des enquêtes et le niveau de contamination admissible prévu aux termes de la loi, on a remarqué la nécessité de prédisposer de différentes activités pour bonifier l'installation et la rendre sûre, qui sont actuellement en phase de projet. Afin de définir les concentrations qui sont le but de la bonification, on a verti la nécessité de réaliser una analyse de risque specifique pour l'installation.

Contaminated Soil '98, Thomas Telford, London, 1998, 691–699

History of the site

The "Officina gas della Bovisa" was since 1908 the main centre for production of gas in Milan. Technological development and, afterwards, the increased availability of natural gas (methane), changed the procedures to produce gas during the years, progressively reducing the industrial activities up to the definitive closure in 1994.

The main production processes utilized: fossil coal from 1908 to 1969, Light Petroleum Derived (LPD) and methane from 1963 to 1994. The first process was obtained by mixing the gas distilled from fossil coal with other gases that were produced through the injection of steam (water gas) or air (air gas) in red-hot coke. In 1963 the first plants for LPD reforming were built. The gas produced was then mixed to the gases from coal distillation and coke gasification. Finally in 1969 the production of gas from fossil coal and coke ended, and was completely replaced by LPD reforming plants and by plants for methane-air mixing.

In 1981 the Municipality of Milan took over from Montedison the direct management of gas service, putting AEM in charge of it and giving AEM the additional job of methanizing the gas service. Therefore from 1984 the distribution of town gas produced in the Bovisa works was gradually replaced with the natural gas supply, and the production plants started being closed, a process that ended in 1994.

The following flows of materials and products characterized the production processes:

Fossil coal distillation process:

RAW MATERIALS (entering the cycle)	PRIMARY PRODUCTS (obtained from raw materials)	BY-PRODUCTS	SECONDARY PRODUCTS (obtained from by-products)
• *fossil coal* • *water*	• *distillation gas*	• *tar* • *coke* • *ammoniac water* • *laming masses saturated with sulphur/cyanides*	• *diluent gas* • *anhydrous tar* • *ammonium sulphate* • *aromatic solvents (benzol, xylene, toluol)*

Catalytic reforming process:

RAW MATERIALS (entering the cycle)	PRIMARY PRODUCTS (obtained from raw materials)	BY-PRODUCTS	SECONDARY PRODUCTS (obtained from by-products)
• *LPD* • *methane* • *water*	• *reforming gas*	• *exhausted catalysts (nickel)*	

Reuse of the site

The site "Officina gas della Bovisa" is subject to a plan for multifunctional urban requalification, including the construction of a new campus for the Polytechnic of Milan, an office district for AEM, residential premises, sports facilities; a vast area will be transformed in public park.

For the urban requalification of the site, the Municipality of Milan (the present proprietor of the area), the Polytechnic of Milan (future proprietor of the part destined to the new Polytechnic premises) and AEM have reached an agreement (Program Agreement), that specifies the new planning of the site (figure 1) and establishes competences, operating procedures and times for its requalification, for what concerns the premises and facilities design and construction, and the soil and groundwater remediation. Such an agreement was promoted by the Region Lombardy.

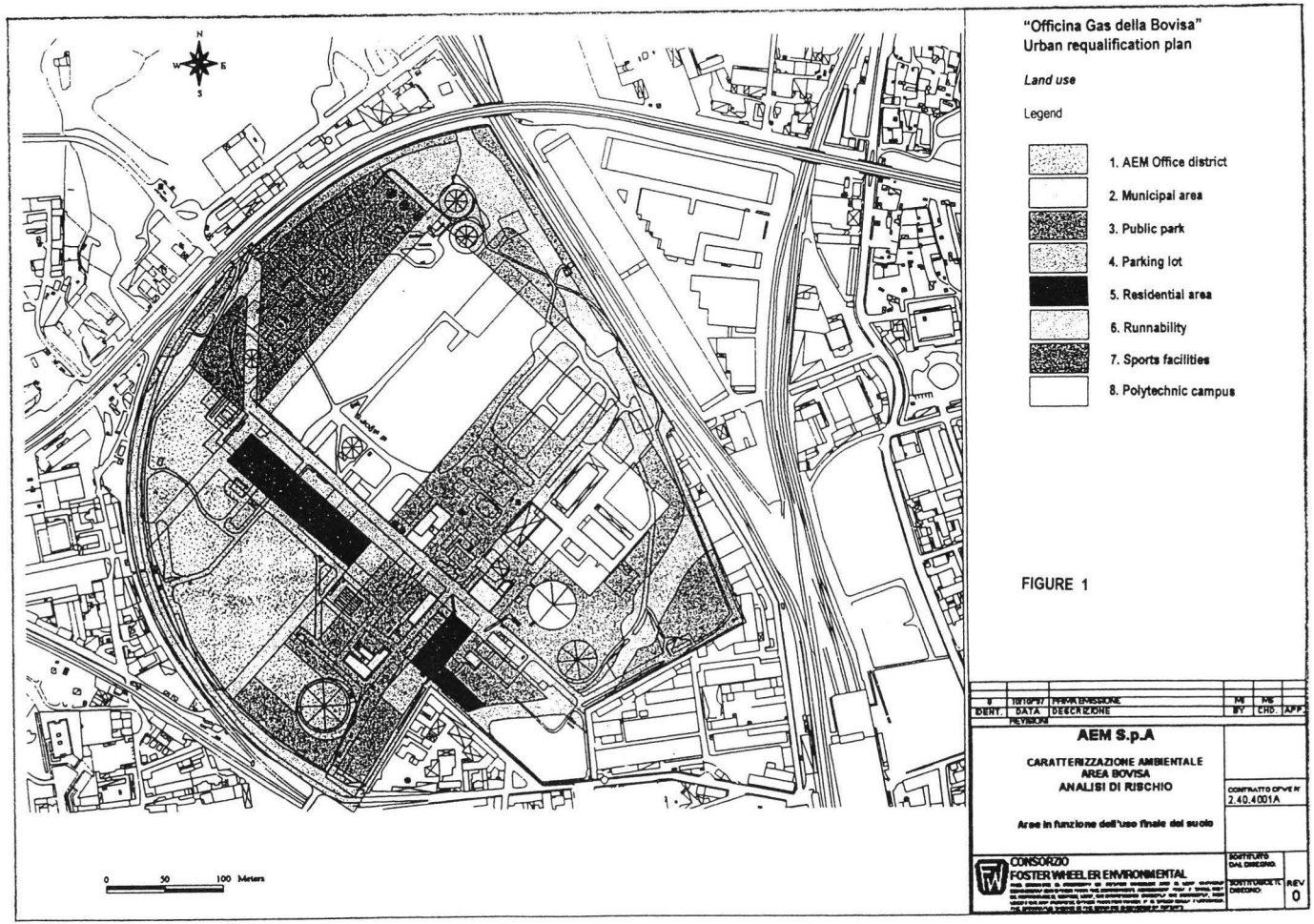
"Officina Gas della Bovisa"
Urban requalification plan
Land use
Legend
1. AEM Office district
2. Municipal area
3. Public park
4. Parking lot
5. Residential area
6. Runnability
7. Sports facilities
8. Polytechnic campus
FIGURE 1
0 50 100 Meters
AEM S.p.A
CARATTERIZZAZIONE AMBIENTALE
AREA BOVISA
ANALISI DI RISCHIO
Aree in funzione dell'uso finale del suolo
CONSORZIO
FOSTER WHEELER ENVIRONMENTAL
REV
0

Figure 1

The commitments for the site remediation have been subdivided among the subjects of the agreement:

- AEM is in charge of environmental investigations;
- the Municipality of Milan has to design and carry out the remediation activities and the hydraulic barrage, expressly required by the Province of Milan;
- the Polytechnic of Milan provides technical support for the above mentioned activities.

Environmental Normative Framework

National level

The new Legislative Decree n. 22 of 5/2/97, that regulates the matter of waste (in place of DPR 915/82), includes a paragraph concerning the remediation and environmental requalification of contaminated sites. The Municipality is responsible for the approval of remediation and containment intervention projects, with mandatory advice of the Region. The Province has to check the execution of works and of environmental investigations. The remediation of sites must refer to the limiting values for soil contamination, that vary according to the use of the sites themselves. Such limiting values have not been fixed yet.

Regional level

The Region Lombardy developed regulations concerning this subject (Decree n. 17252 - 1st August 1996), defining the authorities and procedures for ascertaining the level of soil contamination and for carrying out the remediation, and settling the quality standard of the soils (limiting values). The Region, after having considered the opinion of the Province, is in charge of the approval of the remediation projects. The limiting values are applied to the soil just like it is and to the eluate, and they have been fixed considering the need to protect the ground water from pollution and considering the future use of the sites.

The remediation projects are to be developed on the basis of such limiting values. Nonetheless if limiting values are not considered adequate to the site (as for example when it is technically impossible to reach such values, or when the cost of works would be unsustainable and unjustifiable), the regional regulations admit the possibility of carrying out a specific analysis on the site, and of suggesting limiting values which are different from those in schedule *(risk analysis)*. For what concerns groundwaters, it is necessary to apply also a risk evaluation procedures that have been created by the Provincial Administration.

The normative framework that is being developed, still shows some overlappings of administrative provisions at different levels, in connection with the procedures, authorities and standards of reference. The regional legislation has been adopted to define the remediation project for the Bovisa site (limiting values for the soil and risk analysis procedure).

Environmental Characterization

So as to evaluate the quality of soil and groundwater, AEM carried out several environmental investigations. During these investigations AEM searched for the following parametres:

- Soil: *pH, TOC, cationic exchange capacity, mineral oils, total phenols, cyanides, metals (Arsenic, Cadmium, Lead, Zinc, Copper), PAH (1 Methylnaphthalene, 2 Methylnaphthalene, Acenaphthane, Acenaphthylene, Anthracene, Benzo(a)anthracene, Benzo(a)pirene, Benzo(b)fluoranthene, Benzo(g,h,i)perylene, Benzo(k)fluoranthene, Chrysene, Coronene, Dibenzo(a,h)anthracene,*

Dibenzofuran, Fluorene, Fluoranthene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene) VOC (Benzene, Toluene, Xylens, Ethylbenzene, Styrene, Isopropylbenzene);

- Eluates (with water satured with CO2) and groundwater: *ammonia, total phenols, VOC (Benzene, Toluene, Xylens, Ethylbenzene, Styrene, Isopropylbenzene), mineral oils, PAH (1 Methylnaphthalene, 2 Methylnaphthalene, Acenaphthane, Acenaphthylene, Anthracene, Benzo(a)anthracene, Benzo(a)pirene, Benzo(b)fluoranthene, Benzo(g,h,i)perylene, Benzo(k)fluoranthene, Chrysene, Coronene, Dibenzo(a,h)anthracene, Dibenzofuran, Fluorene, Fluoranthene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene)*

The first investigation was effected in 1995 with the collaboration of EPRI and CISE. It includes taking and analyzing 26 surface samples and 15 depth samples of soil and ground water in order to obtain a general characterization of the whole site. The results showed in some points high levels of contaminants(maximun concentration: total PAH 6270 mg/kg; As 986 mg/kg; Pb 7525 mg/kg; Cn^- 1023 mg/kg; BTEX 840 mg/kg). Such results have been discussed with the competent Authorities:

- USSL (local health authority)
- Province of Milan (competent for water protection against pollution)
- Municipality of Milan (the present proprietor of the area)
- Polytechnic of Milan (the future proprietor and user of part of the area).

On the basis of the above mentioned results, and considering the previous production activities, AEM has agreed with the competent Authorities to carry out further investigations, with the collaboration of specialized companies and laboratories (CISE, Fluor Daniel GTI, Teknodrill, Laboconsult, Chemservice, etc).

On the whole the following investigations have been carried out:

- soil samplings and analyses (535 samples in all) on 160 drillings to a variable depth up to 20 m, to know the areal and depth distribution of the contaminants;
- analysis of interstitial air in 213 points:
- groundwater analysis campaigns, using new piezometers located in significant places to evaluate the contribution to the groundwater pollution due to the more contaminated sub-areas and due to the whole area (uphill/downhill). Analyses have been effected on 66 samples, taken from 38 piezometers to a depth of 30 m and 50 m, and from 2 piezometers to 80 m;
- tests with lysimeters (n. 12) to evaluate the contribution to the groundwater pollution due to infiltration water;
- particle size distribution analyses (about 70)
- pumping tests, 2 of them from a purposely dug well, and 30 Lefranc tests, in order to design the hydraulic barrage, as from the Program Agreement;

The investigations have been carried out with the greatest cooperation of the competent Authorities. As a matter of fact the daily and weekly working schedules were sent in real time to the Authorities. Further, all samples to be analyzed were collected twice, so that each sample could be sent to the Authorities for the later double-check.

Figure 2 shows the investigation points. The total cost of the investigations was about 1 million US$.

The results of the above said investigations showed a distributed overcomings of the limiting values fixed by regional regulation all over the site; the intervention cost for remediaton (about 100 millions US$) sorted out to be absolutely unsustainable and such as to make the new project for urban reuse of the site unrealizable. The groundwater pollution is not very high (maximum concentration of ammonia is 15,3 mg/l and of PAH 4,6 µg/l), almost null. Therefore the hydraulic barrage will not be installed, the ground water will be checked by analyses to be effected every six months, also considering that near the site there are no wells for drinking water.

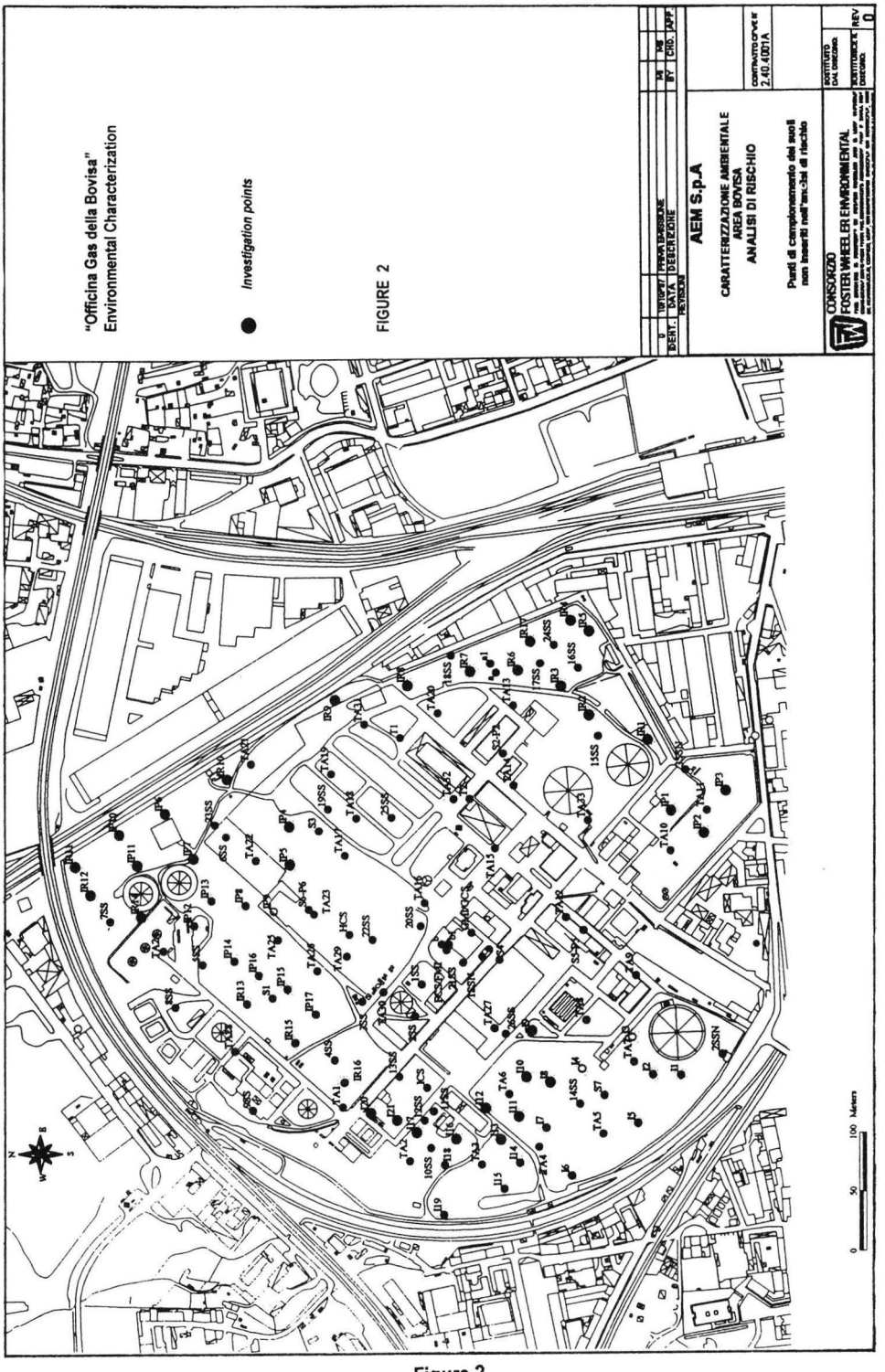
"Officina Gas della Bovisa"
Environmental Characterization
Investigation points
FIGURE 2
AEM S.p.A
CARATTERIZZAZIONE AMBIENTALE
AREA BOVISA
ANALISI DI RISCHIO
Punti di campionamento dei suoli non inseriti nell'analisi di rischio
CONSORZIO
FOSTER WHEELER ENVIRONMENTAL
0
50
100 Meters

Figure 2

Risk analyses

Considering that the intervention cost for remediation is unsustainable on the basis of regional limits, it was necessary to reach an agreement with the above mentioned competent Authorities for a different approach to the area remediation. Since the detected contamination was higher in some small sub-areas (hot-spots), it was decided to carry out a risk analysis, so as to determine the contaminant concentration values specific for the site. This risk analysis was carried out in the period July-December 1997, using the "Standard guide for Risk-Based Corrective Action Applied at Petroleum Release Sites *(RBCA) - ASTM E 1739-95* and with the collaboration of the Foster Wheeler Environmental Consortium.

The RBCA method was applied indirectly, that is fixing the level of acceptable risk (incremental probability of 10^{-5} to contract cancer for cancerogenous substances, and *unitary risk index* for non-cancerogenous substances) and calculating related acceptable concentrations. Risk levels and all the parameters used with this method have been fixed together with the controlling Authorities during preliminary meetings.

The analysis has considered the 73 substances that were searched for during the various investigations. An initial screening on the basis of the values obtained from the concentrations detected and on their toxicity, brought to select 22 indicative substances. The risk analysis has been carried out on such substances. The different destinations of use and the several ways of exposure have been considered: ingestion of soil, dermal contact, inhalation of vapors, inhalation of dust, leaching into ground water. For leaching, it has been calculated the concentration in the soil that assures not to exceed the Italian limits for drinkableness in the beneath ground water (DPR 236/88). Since the Risk Based Screening Levels (RBSL) obtained from tier 1, compared with the analytical data, showed overcomings in too many points, such as to make the intervention cost for clean-up still unsustainable, the method has been deepened to tier 2. We have calculated the Site Specific Target Levels (SSTL), one for each background (8), temporary and future, and for each way of exposure (in total 40 SSTL for each of the 22 indicative substances). Therefore we carried out a synthesis, indicating 4 sub-areas that are homogeneous either for typology of users or for destination of use (1 residence, 2 public park, 3 AEM office district. - Municipality - Polytechnic - 4 road network and parking lot), and selecting the more protective SSTL for the different ways of exposure.

Such SSTL have been compared to the soil analytical data. The ways of transmission characterizing the risk are: dermal contact, accidental ingestion of soil, leaching. The substances characterizing the risk are: Arsenic, Lead, cancerogenous PAH, cyanides, mineral oils and in one point the BTEX (in total 11 substances).

The SSTL so investigated out have been compared whit the similar regional limits (table 1). For cancerogenous substances the values are similar, while for non cancerogenous substances the SSTL are generally higher.

The SSTL have been proposed to the Region Lombardy as derogation of the regional limits. The Region have approved them with an apposite formal act, so that they can be used as a reference for the soil clean-up design..

Preliminary remediation design

The Municipality of Milan (proprietor of the area) with the cooperation of the Polytechnic of Milan and of AEM, is developing the remediation design. Such design settles the technologies that will be used and the volumes of soil to treat in accordance

Indicative substances	Residential land use and sports facilities	AEM Office district, Polytechnic, Municipal areas	*Residential land use*	Public parks	*Park/Agricultural land use*	Parking lots/runnability	*Industrial land use*	Ground water protection	*Ground water protection (high risk value)*
Mineral oils	3,13E+05	4,09E+06	*1,00E+03*	3,13E+05	*1,00E+03*	5,11E+07	*2,50E+03*	6,25E+02	*6,25E+02*
Benzene	2,06E+00	1,44E+01	*1,25E+00*	4,76E+01	*2,00E-01*	2,47E+04	*5,00E+00*	1,50E+00	*1,25E+00*
Toluene	1,57E+02	4,27E+03	*6,25E+01*	1,57E+04	*1,00E+01*	5,11E+06	*2,50E+02*	9,03E+02	*6,25E+01*
Xylens	4,10E+02	1,11E+04	*6,25E+01*	4,05E+04	*1,00E+01*	5,11E+07	*2,50E+02*	2,40E+03	*6,25E+01*
Naphthalene	2,58E+02	7,01E+03	*not-indicated*	2,58E+02	*not-indicated*	1,02E+06	*not-indicated*	3,11E+03	*not-indicated*
Acenaphthane	9,39E+03	3,07E+04	*not-indicated*	9,39E+03	*not-indicated*	1,21E+06	*not-indicated*	1,50E+03	*not-indicated*
Fluorene	6,26E+03	8,18E+03	*not-indicated*	6,26E+03	*not-indicated*	8,09E+05	*not-indicated*	1,37E+03	*not-indicated*
Fluoranthene	6,26E+03	8,18E+04	*not-indicated*	6,26E+03	*not-indicated*	1,02E+06	*not-indicated*	1,10E+03	*not-indicated*
Antracene	4,05E+03	1,06E+04	*not-indicated*	4,05E+03	*not-indicated*	4,18E+05	*not-indicated*	6,40E+01	*not-indicated*
Pyrene	4,69E+03	1,53E+04	*not-indicated*	4,69E+03	*not-indicated*	6,06E+05	*not-indicated*	7,07E+02	*not-indicated*
Dibenzofuran	6,26E+02	8,18E+03	*not-indicated*	6,26E+02	*not-indicated*	1,02E+05	*not-indicated*	4,57E+03	*not-indicated*
Benzo (a) anthracene	1,03E+01	7,84E+01	*1,25E+00*	1,03E+01	*2,00E-01*	9,80E+02	*5,00E+00*	1,87E+02	*1,25E+00*
Benzo (a) pirene	1,03E+00	7,84E+00	*1,25E+00*	1,03E+00	*2,00E-01*	9,80E+01	*5,00E+00*	8,29E+01	*1,25E+00*
Benzo (b) fluoranthene	1,03E+01	7,84E+01	*1,25E+00*	1,03E+01	*2,00E-01*	9,80E+02	*5,00E+00*	9,23E+01	*1,25E+00*
Benzo (k) fluoranthene	1,03E+02	7,84E+02	*1,25E+00*	1,03E+02	*2,00E-01*	9,80E+03	*5,00E+00*	4,92E+01	*1,25E+00*
Chrysene	1,03E+03	7,84E+03	*1,25E+00*	1,03E+03	*2,00E-01*	9,80E+04	*5,00E+00*	3,18E+01	*1,25E+00*
Dibenzo (a,h) antracene	1,03E+00	7,84E+00	*1,25E+00*	1,03E+00	*2,00E-01*	9,80E+01	*5,00E+00*	4,73E+02	*1,25E+00*
Indeno (1,2,3-cd) pyrene	1,03E+01	7,84E+01	*1,25E+00*	1,03E+01	*2,00E-01*	9,80E+02	*5,00E+00*	3,81E+00	*1,25E+00*
Cyanides	3,13E+03	4,09E+04	*5,00E+01*	3,13E+03	*1,00E+01*	5,11E+05	*5,00E+02*	4,96E+01	*not-indicated*
Arsenic	2,00E+01	3,82E+01	*3,00E+01*	2,00E+01	*2,00E+01*	4,77E+02	*5,00E+01*	1,53E+02	*not-indicated*
Lead	4,00E+02	4,00E+02	*3,00E+02*	4,00E+02	*2,00E+02*	4,00E+02	*1,00E+03*	4,00E+02	*not-indicated*
Copper	6,26E+03	8,18E+04	*3,00E+02*	6,26E+03	*2,00E+02*	1,02E+06	*1,00E+03*	6,26E+03	*not-indicated*

Table 1 - Comparison between the various land destinations more protective SSTL (mg/kg) calculated by the ASTM risk analysis (white background) and the corresponding limiting values (mg/kg) fixed by the Lombardy Region regulation (grey background).

with target values fixed by the risk analysis. The design also shows the guidelines to coordinate the engineering and building of the new premises with the clean-up operations, that is: limiting the works underground to minimize the volume of soil to be excavated; reuse as much as possible the excavated soil in the site; possibly place the buildings in non-contaminated or decontaminated areas. On the basis of the site contamination, the following clean-up technologies will be used:

- for the areas with the highest concentration of PAH, metals and mineral oils: on site soil washing, in case with surface-active agents (about 80-100000 m^3);
- for the area contaminated by BTEX: in situ bioventing (about 2600 m^2).

The operations will begin in 1999; they are expected to last 5 years.
In order to complete the definitive clean-up design, further investigations will be carried out in areas that have been little analyzed and some tests concerning the chosen technologies will be executed, in particular a test for on-site biological treatment on soil with a middle-low level of PAH contamination has been scheduled.
In accordance with the preliminary design, the intervention cost for clean-up is about 15 millions US$.

Conclusions

The case of Bovisa is one of the first in Italy for which the clean-up design has been based on the soil contamination limits specific for the site; these limits have been fixed through the risk analysis, as derogation of Region Lombardy limits. That permitted to reduce the clean-up costs, making the interventions possible and allowing to proceed with the area reuse projects.
Depending on the complexity (for example, kind of contamination and multifunctional reuse) and on the extension of the area, the clean-up projects and the building projects are going on side by side, with periodic cross-checks.
The decisions that characterized the remediation process have been taken together with the competent Authorities: a table for technical debates has been created, with increasing reciprocal trust that permitted the continuous progress of works.

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THE SIGNIFICANCE OF AN UTILIZATION-ORIENTED CONTAMINATED SITE MANAGEMENT IN THE COURSE OF INTEGRATED DERELICT LAND USE

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Key words: Abandoned polluted areas, contaminated sites, environmental management, industrial sites, real estate, reuse (of sites), urban areas, utilization concept

SUMMARY

At the increasing complexity measures for reclamation of industrial and military used land, the contaminated site problem is an essential object, since this, on one hand, has tremendous effects on the planned utilization, on the other hand, provides a high risk for the investor. A principle solution of the problem results in the course of an integrated land reuse, for example by translating restrictions resulting from valuation of the contaminated site problems into a common measuring size, whereby easy-to-overlook resistance values (for ex. excess costs in DM/m² caused by remediation demand, necessity for selective dismantling etc.) will be attached to individual lots and shown in a lay-out map.

KURZFASSUNG

Bei den immer komplexer werdenden Vorhaben zur Revitalisierung industrieller oder militärischer Konversionsflächen spielt die Altlastenproblematik eine wesentliche Rolle, da dies zum einen nachhaltige Auswirkungen auf die geplante Nutzung zur Folge hat, zum anderen diese ein hohes Risiko für den Investor darstellt. Eine prinzipielle Lösung des Problems ergibt sich im Rahmen des integrierten Flächenrecyclings, z.B. durch die Umsetzung der Einzelflächen-Restriktionen in eine gemeinsame Meßgröße, wobei den Einzelflächen aus der Bewertung der Altlastenproblematik resultierende (z.B. Sanierungserfordernis, Notwendigkeit zu Rückbau etc.), leicht überschaubare Widerstandswerte (z.B. monetäre Belastung in DM/ m²) zugeordnet und in einen Übersichtsplan dargestellt werden.

Résumé

La problématique des sites contaminés joue un rôle prédominant pour la revitalisation d'anciens terrains industriels ou militaires de part les restrictions quant'à l'utilisation prévue des terrains ainsi que par les risques financiers pour un investisseur qu'ils sont susceptibles d'imposer. Ce problème peut être apréhendé dans le cadre d'une approche intégrée de la revitalisation des terrrains où, par exemple, l'on s'appuira sur des cartes dressées à l'issue de l'étude des pollutions et qui nous donnent, pour les différentes parties du terrain, la charge exprimée par exemple en F/m² pesant sur cette portion de terrrain.

Contaminated Soil '98, Thomas Telford, London, 1998, 701–704

Nowadays, cities, communities and investors are challenged in modern urban planning due to a tremendous amount of ecologically and anthropogenically influenced components and their interaction. In order to meet the urged tasks for adequate reclamation of former industrial or military used real estate, ecologically as well as economically acceptable solutions must have priority for all parties involved. In such integrated planning approaches, the consideration of the contaminated site problem is an essential object, since potentially existing contaminants result in tremendous effects on the planned urban utilization of the real estate concerned.

The experiences of already or still to be performed real estate recycling processes in Germany proved in various negativ-examples, how significant the necessity of the optimization for performance of space- and physical development planning processes is.

In the physical development planning various restrictions, targets and components of other plannings are to be considered, whereby a preliminary roughly devised development is only conditionally realizable resp. may only be mastered by additional staff employment and funds, depending on the extent of the required special planning modifications.

At areas, which were already used especially as industrial or military sites in the past, the potential existence of contaminations or already determined pollutions present an influence extent, which more and more leads to uncertainties. It is often recognized here, that the contaminated site problem is often extremely under- or over-estimated due to for ex. insufficient knowledge of the contamination extent or of the contaminants. So, the contaminations are very often the absolute decision criteria for realization of the entire project.

If contaminations -in the extreme case- are ignored, the healthy living- and working conditions according to §1, para 5, construction law, are no longer guaranteed or result in expensive remediation procedures during realization of the construction. A lot of examples prove this. On the other hand, an over-evaluation and the following prioritized consideration will lead to neglecting of other criteria and planning factors.

As a consequence of this for example, building coverage will not take place at actually suitable areas, but will often be realized in areas without former use, which means on green land. Considering the urgently mandatory landscape protection, this is not the way of future. Target for improvement of this situation must therefore be to classify contaminated sites from the beginning of the planning in an estimated size, so they can be integrated in the planning as one of the „usual" other factors involved.

A principle solution of the problem puts the restrictions resulting from specific contaminated site requirements into a common resistance value, for ex. by translating this into individual lots. This value expresses in direct steps the „resistance" against

planning or reutilization. These „resistance values" may be of different types, like for ex. dimensionless sizes (for ex. resistance 0 = not existing, 1 = low, 2 = high, 3 = extremely high) or other valuable sizes. For the case of translation of selective dismantling of buildings not longer in use and contaminated site problems into a „resistance map" the financial charges of the real estate are offered as common resistance size. By using such financial evaluation sizes (for ex. DM per m²), the effect of the restrictions on the reutilization efforts is presented extremely demonstrative. Figure 1 shows an example.

The target of a such presentation should therefore be to roughly estimate and show easy-to-overlook the financial expense of potential remediation or selective dismantling requirements for the pertinent individual lot. For this, first of all the unspecific contamination potential existing in the individual case must be made clear under consideration of the future utilization scenario. The conditions for this are not only that the pertinent area is sufficiently investigated, which means, sufficient information is available on the contamination potential as well as on the toxicity, mobility, exposure paths etc., but also the availability of an at least rough conception from the investor in regard to the future utilization.

The practice shows, that a contaminated sites expert is -just on basis of long-year experiences on pertinent requirements of the environmental authorites involved- able to evaluate this situation in engineering-technical calculations of the planning- and performance stages mandatory for remediation/securing and to estimate and prognosticate the additional expenses, for ex. per m² already at the very beginning of a project when the present contamination situation is evaluated under consideration of the new utilization. Therefore, the arising total costs for the lot is the simple sum of the purchase price per m² and the excess costs arising from remediation and selective dismantling.

With this conception an instrument will be established at an early stage of time, supporting an early integration in pertinent plannings:

- The timely integration of local authorities and the public enables a frictionless, cost-oriented mastering of the problems from planning view.
- The optimized proceeding of the decision- and planning process allows for a forced project development and -performance.
- The information exchange between the parties involved in the planning process will be intensified.
- Compensation claims arising from planning errors will be avoided.
- As a consequence of the increased transparency, the early and open problem presentation as well as the timely integration of the public positively influence the planning process and support the trust in the plannings.

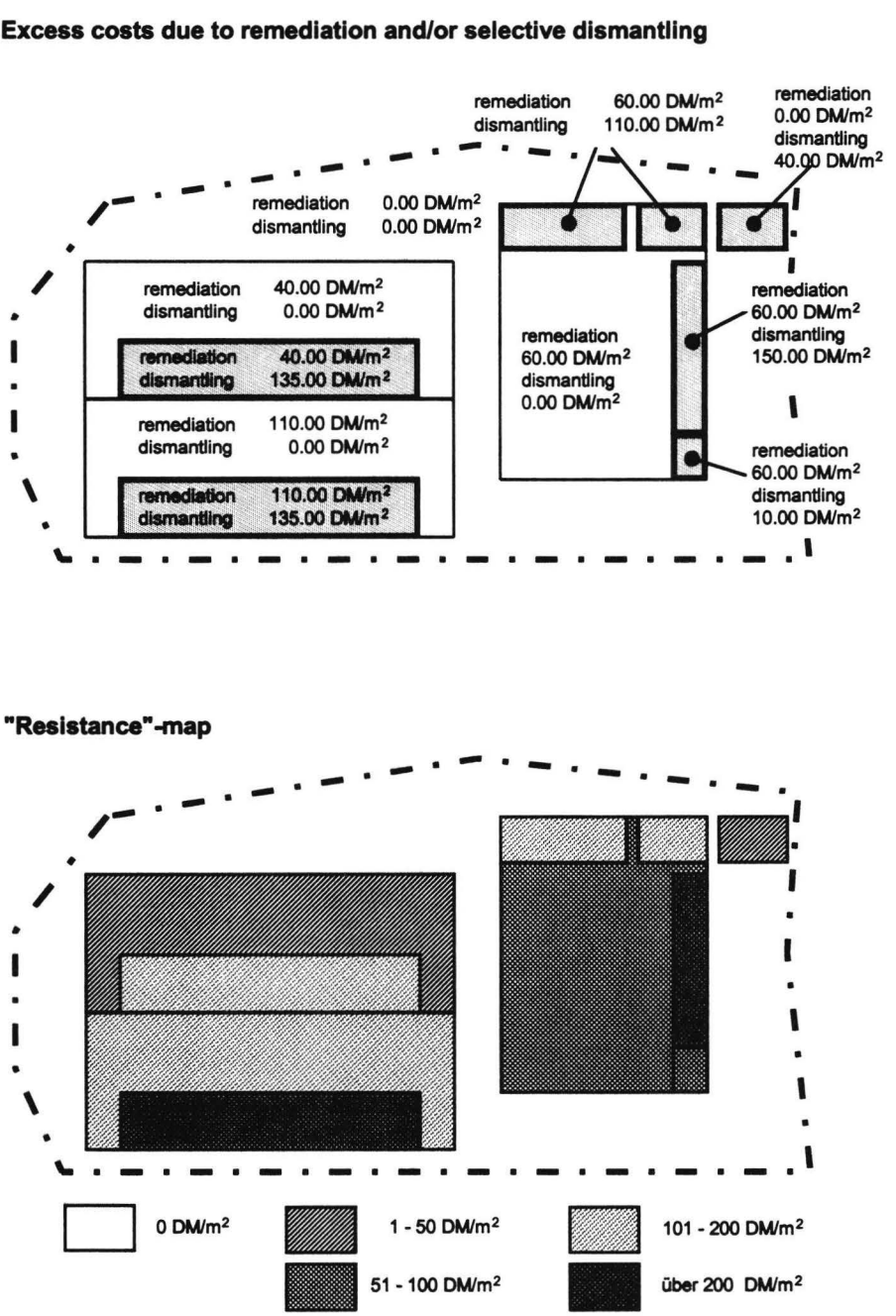

Figure 1: Translation of impacts from remediation and/or selective dismantling in a "resistance"-map

THE UK MARKET PLACE AND CONTAMINATED LAND, REFLECTIONS OF A CONSULTANT

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Key words: due diligence, environmental risks, land register, legislation, liability, risk management,

SUMMARY
Contaminated land has evolved in the last ten years to become a central business issue for a range of property professions. The issue of contaminated land is integrally linked to the markets perception of a site, its redevelopment potential and any potential environmental liabilities which may be associated with it. This paper reviews some of the evolving perceptions and market attitudes to contaminated land and considers some of the challenges for the future in the management of contaminated sites.

RÉSUMÉ:
Pendant les dix dernières années la contamination du sol est devenue une question cruciale pour un nombre de professionels s'occupant d'affaires immobilières. Le problème est lié de façon intégrale à la perception par le marché d'un terrain, les possibilités de redévelopement de celui-ci et les responsabilités vis-à-vis de l'environment qui peuvent y être associées. Ce compte-rendu passe en revue l'évolution des perceptions et de l'attitude du marché, en ce qui concerne les terrains contaminés, et considère les problèmes qu'il y aura à surmonter dans les années qui viennent, au cours de la gestion des sites contaminés.

KURZFASSUNG
Während der letzten 10 Jahre wurde kontaminierter Land ein geschäftlicher Mittelpunkt für eine Reihe beruflicher Bauentwickler. Die Frage von kontaminiertem Land ist eng verbunden mit der Markterkenntnis eines Bauplatzes, dessen Sanierungspotentials und irgendwelche damit verbundenen umweltschützenden Verplfichtungen. Dieser Aufsatz prüft einige der sich entwickeinden Erkenntnisse und Markt-Einstellungen vis-à-vis kontaminiertern Land und erwägt einige künftige Anforderungen in der Leitung von kontanimiertem Land.

Contaminated Soil '98, Thomas Telford, London, 1998, 705–710

The Evolving Regulatory Framework

The last decade in the UK has seen the issue of contaminated land move from the realm of academics and developers addressing site specific issues to an issue engaging a broad range of professionals and an issue which requires to be addressed pro-actively by those involved in the management and transfer of property.

The starting point for the significant growth in consciousness in relation to contaminated land came in 1990, when under the Environmental Protection Act 1990 the government proposed the introduction of a register of potentially contaminated sites. This proposal caused widespread concern about the potential impact such a register might have on land values and the potential for blighting of land in an already depressed property market. The debate that ensued raised the profile of contaminated land and the issue was now being discussed amongst a broad range of professionals including landowners, developers, lawyers advising on land transactions, surveyors, insurers, banks and financiers.

Prior to the proposed introduction of this register the possible presence of contaminated land was largely ignored in any land transaction and remediation was only likely to address the most obvious of problems. Today, however, a property professional would be considered to be negligent if they did not address potential contamination as part of the due diligence process.

Due to the strong opposition to the proposed land register for potentially contaminated sites it was eventually abandoned. Much of the opposition related to the generation of a register for "potentially" contaminated sites. There was a fear that sites might be permanently blighted, even though subsequently they were shown not to be contaminated. At this time there was also no legal definition of contaminated land which would potentially complicate the assessment process.

Following the abandonment of the register the government undertook a further review resulting in the publication of a policy paper "Contaminated Land Clean-Up and Control: Outcome of a Review" which concluded that greater clarity was needed within the law about the clean-up and control of contaminated sites to clarify where environmental liabilities might arise and provide greater confidence within the property market with respect to the management of contaminated sites.

This review was followed by the introduction of legislation in the Environment Act 1995, which sets a framework for the management of contaminated sites. The Regulations enforcing this Act have not yet come into force although consultation documents relating to the likely implementation of the act have been circulated. For the first time this Act introduces a statutory definition of contaminated land in the UK.

Under the Environment Act 1995 contaminated land is defined as :

"any land which appears to the local authority in whose area it is situated to be in such a condition, by reason of substances in, on or under the land that:

a) significant harm is being caused or there is a significant possibility of such harm being caused; or
b) pollution of controlled waters is being , or is likely to be caused."

Under current proposals regulation of these sites will be divided between the Environment Agency (EA) or Scottish Environmental Protection Agency (SEPA) and the Local Authorities with the EA or SEPA having responsibility for "*special site*" which are those considered to be of particularly high risk. The relevant authority will have the powers to require the responsible person to mange the risk associated with land contamination at the site. Details of all sites defined as contaminated under the Regulations will be held on a publicly available register.

It is not the intention of this paper to describe in detail the implications of this legislation. There are however a number of key philosophies around which the legislation is based which will have implications for the future management of contaminated land in the UK.

- contaminated land will now be defined on the basis of a risk based approach;
- remediation of contaminated sites may be required by the regulatory authorities but this must be based on a "*suitable for use*" approach;
- whereas previously the liability for management or clean up of a contaminated site rested with the site owner, the new Act has provisions for enforcing a polluter pays principal where the polluter or polluters can be identified;
- the emphasis of the legislation is that remediation should be development led and as far as possible incorporated into plans for redevelopment of the site;
- there are provisions for allowing the cost-benefit of remediation to be taken into account.

The most significant shift in the governments approach has been from focusing on "potentially" contaminated sites to defining contaminated land within a risk based framework. Although there is still debate to be had on the interpretation of words such as "*significant harm*" and "*significant possibility*" the act places the focus clearly on the high risk sites and leaves a significant number of sites outwith the statutory definition of contaminated land which would formerly have been considered as such.

SEPA has estimated that of the total area of 13,025 hectares of land identified as being potentially contaminated in Scotland as part of previous surveys, between 5,000 and 10,000 hectares may come under the statutory definition of contaminated land (38% to 76%), while only in the region of 3 to 5% will be classified as special sites.

The Impacts on the Property Market

Despite the growing awareness of contaminated land as an issue there is still a lack of confidence in the process of managing contaminated sites within the property market. The government have over the past five years published a plethora of guidance documents on the management and remediation of contaminated sites in the hope of ensuring a more unified approach to the issue, however inconsistency remains, which is in many cases driven as much by perception as science.

For example at one level there are banks in the UK which will not lend on any property whether potentially contaminated or otherwise until an environmental review has been conducted as part of the due diligence process. On the other hand there are still examples of transactions where no account is taken of the potential presence of contamination. There are also many examples of sites which have been subjected to full scale remediation which would not have been required on the basis of a risk assessment but was undertaken to improve the marketability of the site. In these cases the design of the remediation scheme has been driven as much by market perception of the risk as by a scientific evaluation. This situation is particularly prevalent in relation to potentially emotive contaminants such as PCBs, radioactivity or asbestos, or where the former use of the site might be considered to have been potentially highly contaminative. These types of sites are also often emotive to local residents, thus further blighting a potential development site.

It can loosely be demonstrated that the degree of uncertainty associated with knowledge on the potential contamination at a site is often proportional to the degree to which environmental issues effect land values. The more clearly the levels of contamination at a site can be defined the better able are bankers, insurers, accountants and their advisors to evaluate the risk. As the amount of information about the site increases the number of unknowns decease and in turn the perception of risk. In recognition of this a growing number of vendors are undertaking an environmental assessment of contamination at a site prior to placing the site on the market in the hope of allying potential fears as early as possible. This may in some cases be purely a desk based evaluation or in instances where there is a high degree of uncertainly associated with the possible extent of contamination at a site a full site investigation may be undertaken.

As long as this uncertainty remains there will continue to be blighted sites which remain undeveloped, a situation which is contrary to the sustainable use of land and does not ease the pressure on our green belt sites.

It is not clear at the moment whether the new proposals for management of contaminated land will provide the framework required to boost market confidence. There should be apparent benefits for those sites which are not defined as contaminated under the statutory definition and therefore remain off the register. Former industrial sites may still have levels of contamination above

those of green field sites which require management during the development process yet the potential fear of liability should have been removed.

For the remaining sites the important issue is to provide market confidence through the remediation process. This process needs to be fully documented to a standard which will survive third party scrutiny and provide confidence to all those involved. The remediation process must also be seen as one which survives the test of time and will remain an important part of the sites documentation which can then be referred to in the event of future changes at the site. All to often documents are of poor quality and have not been fully maintained and much re-work is required at a future point of sale or redevelopment.

Challenges for the Future

Clearly there is still a significant challenge to ensuring that contaminated sites are addressed within a consistent framework and the presence of potential or actual contamination does not hinder the redevelopment and marketability of sites. Dealing with contaminated sites should be seen as a process of managing an issue rather than a problem. There is now an established group of professionals with experience of managing contaminated sites and assessing risks and a large amount of guidance which if followed should ensure consistency of approach. There are a number of issues which require to be addressed in relation to ensuring the marketability of contaminated sites is maximised in the future.

- Consistency - there is still a considerable degree of variation in the way that the risk from a contaminated site is evaluated and communicated. The degree of risk may be evaluated differently by different professionals. Further guidance on the definition of "*significant harm*" and "*significant possibility*" are required together with a consistent approach from both consultants and regulators to ensure this is achieved.

  Education - there is still a considerable problem relating to perception of contamination. A process of education of both the public, where local communities are involved and property professionals is required, to ensure actual and perceived risk can be separated. This will be assisted if the management of the process more pro-actively involves all parties with an interest in the site throughout the evaluation and remediation process.

- Documentation - the presence of a register of contaminated sites should in theory assist in supporting some of the above issues. Once a site is on a register there will be a recognition that a liability exists which the company involved will then be required to manage. What is however of paramount importance is that the register is well maintained and updated. There are sophisticated tools such as geographical information systems (GIS) which could be developed to create registers of sites which can be effectively updated and used as a much broader planning tool. Whether appropriate levels of investment are applied to the development of these registers to ensure they

utilise state of the art technology and thereby become an investment for the future remains to be seen.

Conclusions

Effective communication and documentation are a large part of building confidence in the process of evaluation and management of contaminated land. The framework for the management of contaminated land might be argued to have become more clear yet there are still challenges in its effective implementation. A number of questions remain to be asked. Will the presence of a register of sites cause blight or will it in fact increase market confidence in the process of managing contaminated land? Will this achieve the aim of removing certain sites from the definition of contaminated land allowing their successful redevelopment without the need for unnecessary costly remediation?

It is to be hoped that this process will remove blight from low risk sites and will allow the effective management of high risk sites as an effective part of the redevelopment process thus increasing the marketability of brownfield sites and ensuring lasting solutions for their management.

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MANAGING RISKS OF CONTAMINATED SITES - THE POINT OF VIEW OF A BANKER VERSUS THE POINT OF VIEW OF AN ENGINEER

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Key words: Credit Approval Process, Solvency Risks, Collateral Risks, Environment Desk Corporate Banking, Site Management, Investigations, Risk analysis

SUMMARY

Environmental issues form an integral part of the credit approval process in UBS's corporate finance in Switzerland. One of the issues are risks from contaminated sites. Based on the legal regulations in Switzerland they can be categorised into two groups: solvency risks and collateral risks. These risks have an effect on the property value.
We shall explain what instruments we have established at UBS to identify contaminated sites and to evaluate the significance of risks. We will speak about difficulties and highlights of the cooperation between the advisory unit - the Environment Desk Corporate Banking - and engineers. We will show how the results of the engineer's site assessment are incorporated into the overall assessment of the borrower's credit standing.

KURZFASSUNG

Bei der UBS ist die systematische Beurteilung von Umweltrisiken ein Bestandteil der Bonitätsprüfung von Kreditnehmern aus dem schweizerischen Firmenkundengeschäft. Die von Altlasten ausgehenden Risiken können dabei in zwei Gruppen eingeteilt werden: Bonitätsrisiken und Besicherungsrisiken. Beides führt zu einer Wertminderung.
Ausgehend vom Umweltkonzept der UBS für das Kreditgeschäft und Erfahrungen wird gezeigt wie unsere Instrumente aussehen, um Altlasten zu erkennen und zu bewerten. Die Verantwortlichkeiten und die Erwartungen an unsere Kunden werden dabei verdeutlicht. Die Ergebnisse der Prüfung fliessen in die Bonitätsbeurteilung ein und wirken sich auf die Belehnungshöhe, Tilgungsdauer und Zinshöhe aus. Hier wird ersichtlich, dass ein Finanzinstitut den Risikobegriff anders versteht als ein Umweltberater.

RÉSUMÉ

Les questions environnementales sont inhérentes au processus d'approbation de crédit dans le domaine du financement des sociétés de l'UBS en Suisse. Relatif à la loi fédérale suisse, les risques posés par des sites contaminés peuvent être classés en deux groupes: risques de solvabilité et risques collatéraux. Ceci a un effet sur la valeur immobilière.
Cet article décrit les instruments d'identification des sites contaminés et d'évaluation de l'importance de ces risques établis par l'UBS. Les difficultés et les points saillants d'une coopération entre l'unité consultative - les services bancaires aux entreprises du bureau de l'environnement - et les ingénieurs sont également élucidés. Les résultats de l'évaluation obtenus par l'ingénieur sont intégrés dans l'évaluation globale de la réputation de solvabilité de l'emprunteur.

Contaminated Soil '98, Thomas Telford, London, 1998, 711–716

The principle

UBS (Union Bank of Switzerland) has resolved to take full account of environmental considerations in both its internal operations and its actual banking business by introducing a comprehensive environmental policy. It has taken this step in response not only to the new environmental awareness in society at large, to environmental legislation and the hazards resulting from a failure to address environmental issues, but also to the opportunities presented by environmentally aware business activity.
Higher priority is now being given to the consequences of contaminated sites not only as a result of greater public awareness, but also because of accelerated structural change and the difficult economic situation in Switzerland. The issue of contaminated site carries with it significant environmental and therefore economic implications.
From a legal point of view, the risks associated with contaminated sites may be divided into two categories:

1. The risk of non-repayment of loans in cases where due to an impact on health and environment immidiate site remediations are imposed by the authorities or where compensation is claimed by injured parties, resulting in major financial consequences for the borrower. These third party claims affect the status quo.
2. Risks to collateral where site pollution impairs the future exploitation of a property or where it can only be fully used after substantial remedial investment. Both factors reduce the value of the property.

Contaminated sites risk assessment will therefore arise both when examining the borrower's financial standing for unsecured loans and when considering loans secured by a property mortgage.

Procedure of Identification

Responsibility for early identification of possible environmental risks lies with our Corporate Client Advisers. They are specially trained for their job, and the necessary tools are placed at their disposal. In addition, an internal environmental advisory service has been established: the Corporate Banking Environment Desk. This backs up the Corporate Client Advisers and is available to conduct more detailed investigations and valuations. The Registers of Suspected Contaminated Sites as currently maintained by certain Cantons in Switzerland are of only limited significance in this context. Although they may alert the lender to potential risks, they do not constitute a basis for credit decisions. Personal experience, expertise, technical resources and, above all, inspection of the property are the means by which any suspicions are confirmed or allayed. Only the publicly accessible Registers of Contaminated Sites, prepared on the basis of the revised Environmental Protection Law, will in future rectify the situation. Credit institutions will then be in a position to accurately identify any risks and to specify appropriate remedial action. For their part, those adversely affected will be spared the unpleasant consequences of misinterpretation.
Where a polluted site is the subject of specific suspicion, the borrower should prepare an environmental site assessment report. It brings several benefits. It creates transparency

and enables the lender to understand the risk situation and to assess it with reasonable accuracy. From the point of view of the lender the main contents of a site assessment report should be not only results of historical and scientific investigations of the site. The emphasis must lay on economic issues. Valuation must otherwise be performed by the lender on the basis of individual experience of the extent of potential damage, remediation measures required if full statutory orders are fully implemented, and the cost of waste removal. Cooperation between the affected party and the authorities gives the audit greater credibility. It becomes even more urgently necessary if there is a danger of impact to the environment or to adjoining sites (third party claims).

Environmental Site Assessment

The interests of the banks, which have currently become an additional partner, are manifold (see ahead). They focus primarily on the remediation costs and, thereby, on the solvency of a borrower. However, similarly to the insurance companies, the banks are also interested in sustainable remediation measures.
The interests and requests of the various partners (authorities, owners of contaminated sites, insurance companies, etc.), which are involved in the contaminated site management are often diverse, however, they have to be considered in site assessment:

- The contaminated site owners are mainly interested in finding a favourable solution to their remediation problems. The environmental risks are often of secondary importance to them.
- The insurance companies are interested in the cost factors and in sustainable remediation measures.
- The authorities and the society are more interested in the environmental risks and less in the remediation costs of a contaminated site.

The following figure illustrates the different interests of the various parties involved.

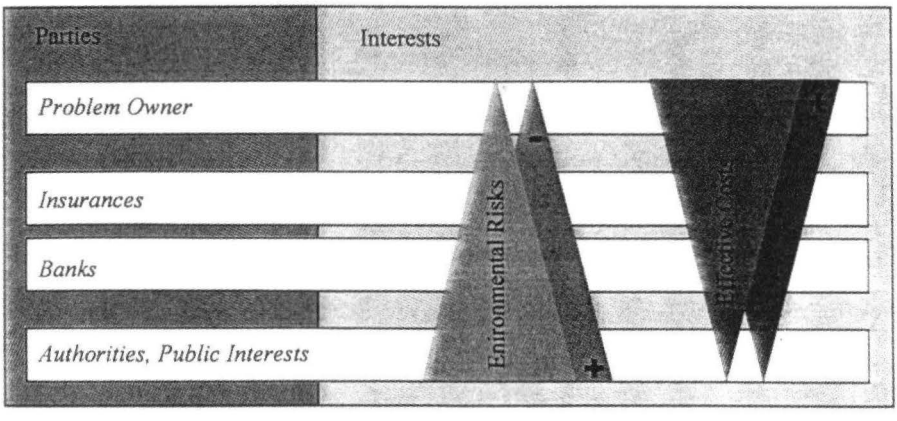

Figure 1: "Different Interests of the Parties involved"

The different interests and demands constitute a considerable challenge to the engineer who will have to take them into account in site assessment.

Contaminated Site Management

Figure 2 describes the generalised site management procedure as used in Switzerland and, with some differences, also in other countries.

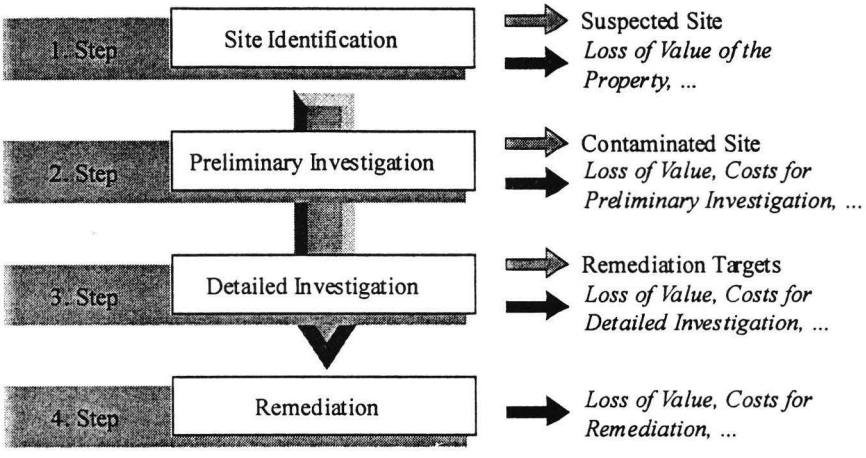

Figure 2: „Site Management Procedure and financial Impacts"

After the steps site identification, preliminary investigation and detailed investigation risk evaluations shall follow. Based on these evaluations various measures are proposed. The measures put into practice are certainly of relevance to the owner: 1. The *suspected* site or CONTAMINATED site is registered by the authorities as suspected or contaminated site in a *non-public* or PUBLIC Cantonal Register. 2. The value of the property is reduced. Costs for further investigations and monitoring, remediation measures (decontamination or containment measures) are the consequences (Fig. 2).

The engineer in the area of conflict between owner, authority, insurances and banks

The objectives of an engineer are the management and the reduction of the environmental risks of a contaminated site based on scientific knowledge, the legislation and the interests of the contaminated site owner. The interests and requests of the mentioned parties too have to go into the work done by the engineer (Fig. 1). The parties different points of view will raise problems and conflicts for the engineer:

authorities, public interests versus engineer

- Legal uncertainties: E.g. site specific remediation versus equal rights and duties. ⇒ There is a need for legal remediation targets and levels.
- Cantonal federalism: the different cantonal site management and implementation of the Swiss Legislation for the

	contaminated sites cause difficulties. • Lack of information and knowledge: Involved third parties need more information.
banks, insurances versus engineer	• Different language: Insurance risks financial risks versus environmental risks • Different objectives: Reduction of costs and unendangered credits versus the reduction of environmental risks • Consultants have to foresee or to plan decisions made by the authorities and to review the consequences and measures, which will follow.
site owner versus engineer	• Costs for remediation versus environmental risks • Difficulties with demanded favourable expert opinion

Beneath the difficulties and conflicts shown above, today the consultant has additionally more general problems:

- Tough competition (⇒ trade liberalisation, recession, etc.), pressure of costs
- Difficulties with liabilities
- New legislation (e.g. liberalisation of trade act, etc.)
- Perhaps image problems too

The mentioned difficulties and conflicts represent boundary conditions for the engineer and accompany him in his daily work. Nevertheless the consultant has to be aware of the circumstances that risks of site owners are also risks of banks. Therefore, the demands of banks are as important as demands and requests of other parties.

The financial assessment

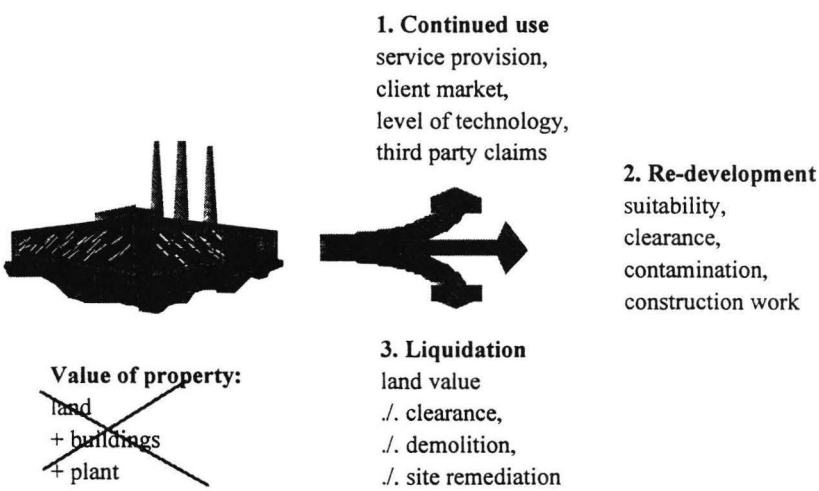

Figure 3: „Assessment of Enterprises"

In the case of commercial and industrial properties, site pollution risks are assessed with reference to the continuation of current use and to the potential for alternative uses, such as re-development or closure of the business (Fig. 3). The property is treated as a production centre of goods or services for which market demand exists. Anticipated revenues from continuation of the business may be reduced by third-party claims arising from pollution (civil or statutory claims unrelated to building plans). If the market no longer requires the goods or services, the production site has to be put to new use. If the existing buildings can be re-used (re-development), the cost of remediation will inevitably result in a reduced valuation. In the case of highly specialised property, re-development is only possible after demolition and total remediation of the site (liquidation), measures which involve considerable waste disposal costs (Federal Waste Disposal Law). Loans must therefore be amortised within a period determined by market forecasts to at least the adjusted market value or liquidation value (Fig. 4). The net asset value is not the determining factor for any financing. Cash-flow considerations have priority.

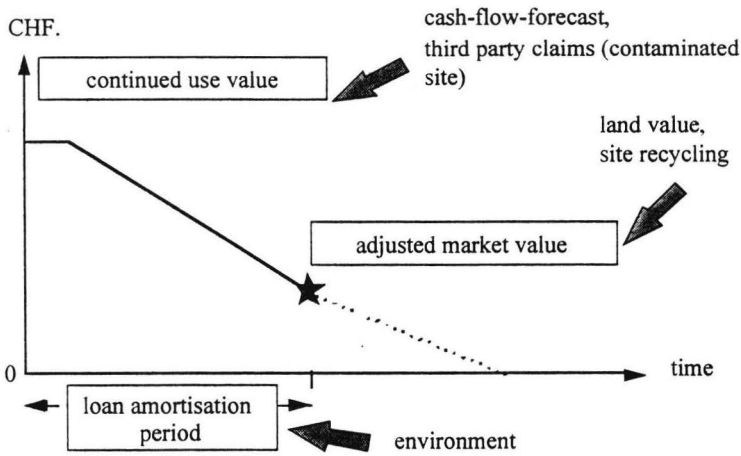

Figure 4: „Lending Criteria for industrial & commercial Property"

Conclusion

A contaminated site does not have to be a catastrophe for the borrower. The decisive factor from the lender's viewpoint is the ability to assess the risks attached to a site. This calls for complete transparency and openness on the part of the borrower.
The application of ecological criteria as an additional factor in the assessment of creditworthiness is not simply a reaction to society's current and future ecological demands. It also reflects UBS's acceptance of its environmental responsibilities. UBS's approach will continue to be governed by these universal criteria.

Quintessence: Transparency and cooperation among all involved parties is the key to success. And after all financial aspects are important; they lead to a proactive environmental management wherewith banks contribute to the environmental protection.

Index of keywords

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