INTRINSIC DECHLORINATION OF 1,2-DICHLOROETHANE AT AN INDUSTRIAL SITE

Tom N.P. Bosma, *Martine A. van Aalst-van Leeuwen, Jan Gerritse, and Erwin van Heiningen*
(TNO, Apeldoorn, The Netherlands)
Jan Taat (Delft Geotechnics, The Netherlands)
Marc Pruijn (Heidemij Realisatie, The Netherlands)

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

Contaminated Soil '98, Thomas Telford, London, 1998, 197–202

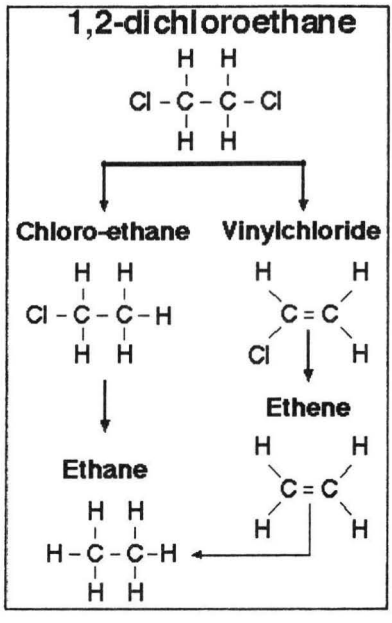

FIGURE 1. Transformation pathways of 1,2-DCA under sulfate reducing and methanogenic conditions.

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

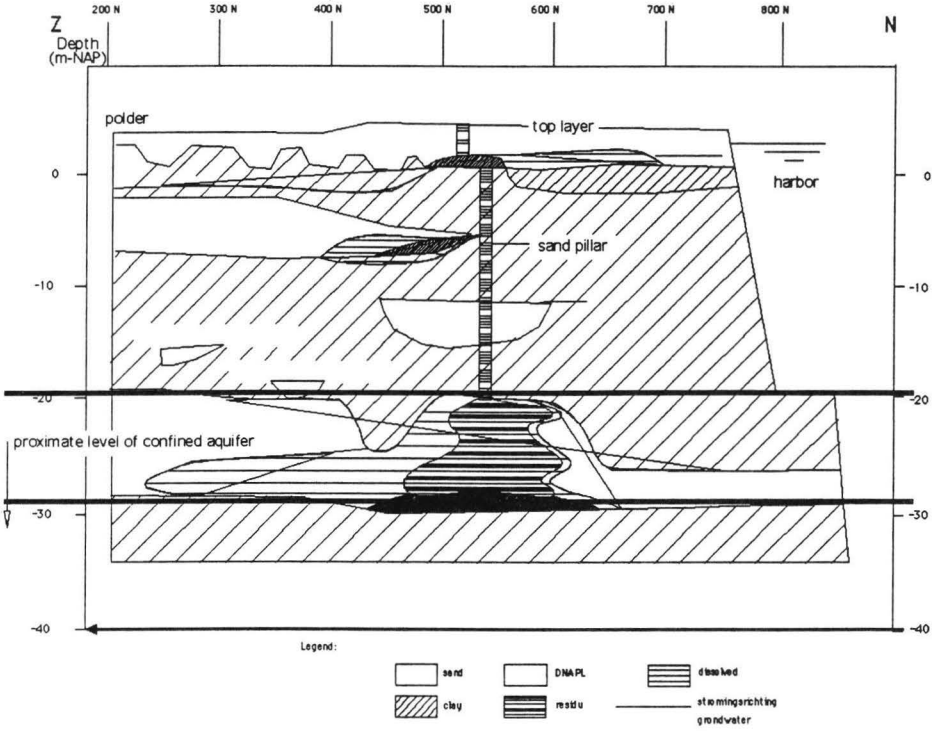

FIGURE 2. Cross-sectional view of the site (left: south; right north) and the vertical distribution of 1,2-DCA.

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

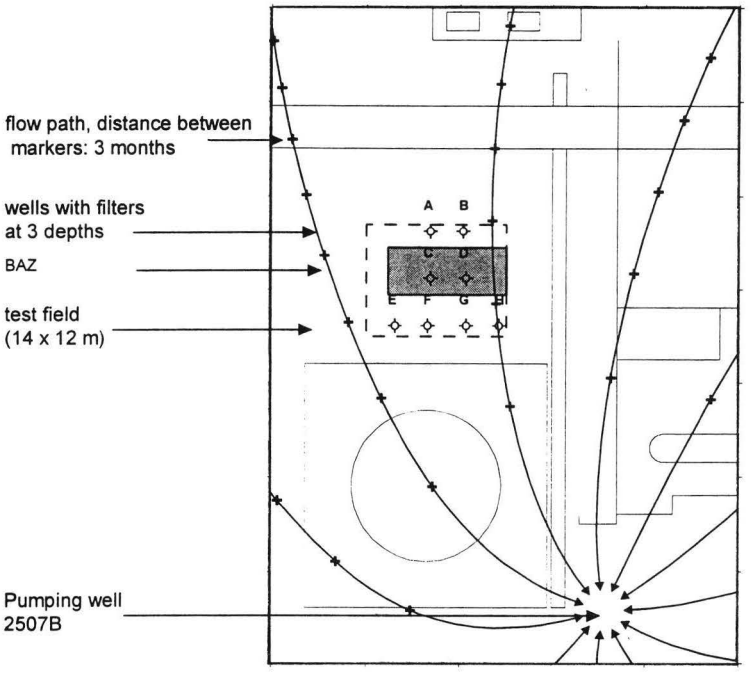

FIGURE 3. Plane view of the test field. The size of the location is about 10x15 m.

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

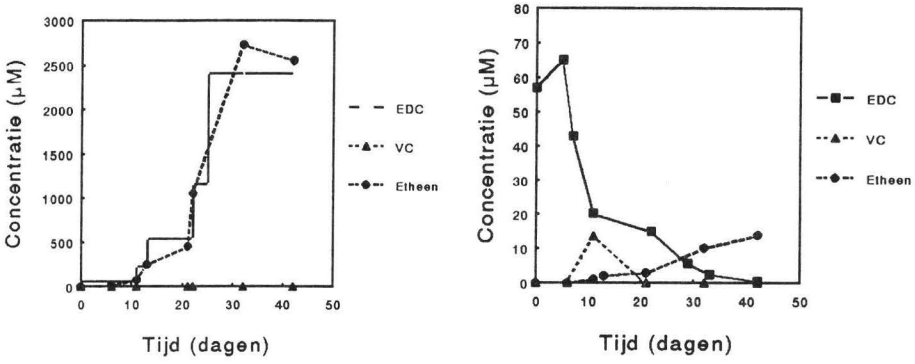

FIGURE 4. Spontaneous biotransformation of 1,2-DCA in samples from the pumping wells (A) and enhanced biotransformation in samples from the test field (B). No spontaneous biodegradation was observed in the samples from the test field (not shown).

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.

REFERENCES

Belay, N. and L. Daniels. 1987. Production of ethane, ethylene and acetylene form halogenated hydrocarbons by methanogenic bacteria. Appl. Environ. Microbiol. 53:1604-1610.

Bjerg, P. L., R. K., J. K. Pedersen, and T. H. Christensen. 1995. Distribution of redox sensitive groundwater quality parameters downgradient of a landfill

(Grindsted, Denmark). Environmental Science & Technology. 29(5):1387-1394.

Bosma, T.N.P., van Aalst, M., Rijnaarts, H.H.M., Taat, J. and Bovendeur, J., 1997. Intrinsic dechlorination of 1,2-dichloroethane at an industrial site. In: R.E. Hinchee (Editor), Bioremediation. Battelle Press, Columbus, Richland, pp. 155-160.

Egli, C., Scholtz, R., Cook, A. & T. Leisinger. 1987. Anaerobic dechlorination of tetrachloromethane and 1,2-dichloroethane to degradable products by pure cultures of Desulfobacterium sp. and Methanobacterium sp. FEMS Microbiol. Lett. 43:257-261.

Janssen, D.B., Scheper, A. and B. Witholt. 1984. Biodegradation of 2-chloroethanol and 1,2-dichloroethane by pure bacterial cultures. Prog. Ind. Microbiol. 20:169-178

Jeffers, P.M., L.M. Ward, L.M. Woytowitch and N.L. Wolfe, Homogenous hydrolysis rate constants for selected chlorinated methanes, ethanes, ethenes and propanes, Environ. Sci. Technol., (1989), 23(8).

Wijngaard van den, A.J., van der Kamp, K.W.H.J., van der Ploeg, J., Pries, F., Kazemier, B. and D.B. Janssen. 1992. Degradation of 1,2-dichloroethane by Ancylobacter aquaticus and other facultative methylotrophs. Appl. Environ. Microbiol. 58:976-983