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NATO/CCMS Pilot Study

Evaluation of Demonstrated and Emerging Technologies for the Treatment and Clean Up of Contaminated Land and Groundwater (Phase III)

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Special Session

Monitored Natural Attenuation

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NORTH ATLANTIC TREATY ORGANIZATION

NATO/CCMS Pilot Study

Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater (Phase III)

1999 Special Session
Monitored Natural Attenuation

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Contents

Introduction

The Council of the North Atlantic Treaty Organization (NATO) established the Committee on the Challenges of Modern Society (CCMS) in 1969. CCMS was charged with developing meaningful programs to share information among countries on environmental and societal issues that complement other international endeavors and to provide leadership in solving specific problems of the human environment. A fundamental precept of CCMS involves the transfer of technological and scientific solutions among nations with similar environmental challenges.

The management of contaminated land and groundwater is a universal problem among industrialized countries, requiring the use of existing, emerging, innovative, and cost-effective technologies. This document provides a report on the special session on monitored natural attenuation (MNA) from the second meeting of the Phase III Pilot Study on the Evaluation of Demonstrated and Emerging Technologies for the Treatment and Clean Up of Contaminated Land and Groundwater. The United States is the lead country for the Pilot Study, and Germany and The Netherlands are the Co-Pilot countries. The first phase of the pilot study successfully concluded in 1991, and the results were published in three volumes. The second phase, which expanded to include newly emerging technologies, concluded in 1997. Final reports documenting 52 completed projects and the participation of 14 countries were published in June 1998. Through this pilot study, critical technical information is made available to participating countries and the world community.

The Phase III study focuses on the technical approaches for treating contaminated land and groundwater. This includes issues of sustainability, environmental merit, and cost-effectiveness, in addition to continued emphasis on emerging remediation technologies. The objectives of the study are to critically evaluate technologies, promote the appropriate use of technologies, use information technology systems to disseminate the products, and to foster innovative thinking in the area of contaminated land.

The first meeting of the Phase III study was held in Vienna, Austria, on February 23-27, 1998. The meeting included a special technical session on treatment walls and permeable reactive barriers. The proceedings of the meeting and of the special technical session were published in May 1998.

The second meeting of the Phase III Pilot Study convened in Angers, France, on May 9-14, 1999, with representatives of 18 countries attending. Ten of the participating countries presented 15 projects. These projects were discussed and commented on by experts. Five new projects were also proposed and selected for inclusion in the study. A special technical session on monitored natural attenuation was held and is the focus of this report. The general proceedings of the 1999 annual meeting are available in a companion publication.

This publication is the report from the special session on monitored natural attenuation. This session was chaired by Fran Kremer, Ph.D. of the U. S. Environmental Protection Agency and Anja Sinke, Ph.D. from the Dutch TNO Institute of Environmental Science. This report contains the papers presented at the MNA session and recommendations developed by the co-chairs.

This and many of the Pilot Study reports are available online at *http://www.nato.int/ccms/*. General information on the NATO/CCMS Pilot Study may be obtained from the country representatives listed at the end of the report. Further information on the MNA report can be obtained from the specific authors.

Stephen C. James
Walter W. Kovalick, Jr., Ph.D.
Co-Directors

General Overview

This report includes the papers presented at the NATO/CCMS Pilot Study Meeting in Angers, France, May 9-14, 1999, for the special session on Monitored Natural Attenuation (MNA). This is the Phase III of the Evaluation of Demonstrated and Emerging Technologies for the Treatment and Cleanup of Contaminated Land and Ground Water.

Internationally, overall, there is an increased understanding of the naturally-occurring transforma-tion processes to decrease the toxicity, mobility and/or volume of hazardous contaminants. This understanding is opening the door for some regulatory agencies, internationally, to begin to consider how MNA can play a role in site remediation activities.

For those contaminants which are amenable to biodegradation, the key question is the rate at which these contaminants can be degraded. The rate is determined by a number of factors. To determine whether MNA is appropriate in these circumstances depends upon whether the appropriate environmental conditions are suffi-cient to sustain adequate rates of degradation to ensure compliance with the cleanup goals within a given period of time.

The most prevalent use of MNA is focused on petroleum hydrocarbons, solvents and metals. From a research venue, in the laboratory and in the field, work is continuing to more fully understand factors such as the microbiology, hydrogeology and geochemistry's role in attenuating a variety of contaminants.

Internationally, there is a wide disparity in the development of policy and technical guidance, implemen-tation of MNA and ultimately the acceptance of MNA. Some countries are very reluctant to consider it's use, others are considering limited applications, and still others have instituted formal technical guidance and policies. One of the key determinants is the timing for the need of the impacted resource. In some areas, the impacted resource will be needed before MNA can achieve clean-up goals. Another determinant is, given the environmental conditions, the degree of confidence that the attenuating mechanisms will adequately protect human health and the environment.

As further field research is conducted with various contaminants under various environmental conditions, the international scientific community and those directly involved in site remediation activities will gain a better understanding of the role that naturally-occurring processes play in remediation. This understanding will be fostered by the continued exchange of information as well as conducting collaborative field research to further elucidate the attenuating processes and to define the most appropriate indicator parameters to moni-tor the processes.

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Monitored Natural Attenuation of a Municipal/Industrial Landfill Leachate Plume - Approaches, Issues, and Challenges in Applying Current U. S. EPA Guidance (J. F. Barker and L. Austrins, University of Waterloo, Canada)

Abstract

A landfill leachate plume developed in a complex sand/gravel/clay-till aquifer system from a landfill that received both municipal and industrial waste from about 1960 to 1979. Wells up to about 0.6 km down gradient of the landfill had been contaminated and replaced. The risk was that additional down gradient wells would become contaminated. Chemicals of concern included benzene, 1,2-dichloroethane, acetone, isopropanol, methyl-isobutyl-ketone, and tetrahydrofuran. Groundwater sampling with supporting laboratory microcosm testing provided the basis for anticipating the likely natural attenuation of the chemicals. Contamination was found to extend about 1.2 km down gradient and to a depth of 60 m below the water table. Biodegradation and dispersion are the active attenuation mechanisms. The risk to other wells seems very low, but the landfill source remains and some chemicals are likely to migrate > 2 km before concentrations fall below target levels. While the authors feel comfortable that monitored natural attenuation (MNA) is an appropriate remedial approach at this site, issues such as a continuing landfill source for the plume, a potentially expanding plume for some chemicals, and a large water resource being degraded, raise concerns when applying the EPA's OSWER Directive 9200.4-17, various site-specific, risk-assessment-driven "no action" alternatives, and other developing protocols.

Introduction, Hydrogeology, Chemicals of Concern

An informal dump operated on the site from about 1955 to 1960, becoming a sanitary landfill in 1960, then a county-wide landfill of approximately 65 acres, accepting commercial and industrial waste from 1968. It was closed in May, 1979 when organic contamination was found in domestic groundwater wells up to almost 600 m down gradient of the site. Impacted wells were replaced by a piped water supply and by deeper wells. Surface discharge of groundwater is likely many 10's of km down gradient.

The site is located in glacial deposits overlying an unconfined and partially confined aquifer comprising generally thick (> 20 m) sand and gravel units interbedded with relatively thin (< 6 m) clayey units. The plume appears to occupy a broad depth of the aquifer and is not restricted simply to high-conductivity lenses (see section, Figure 1). The chemical plumes appear reasonably regular at the field scale, based on groundwater sampling every 3 m during drilling.

The water table slopes consistently to the west from the landfill site (section, Figure 1). Chloride, considered a conservative tracer of landfill leachate, forms a plume identified by above- background Cl concentrations (> 20 mg/L) that extends at least 1200 m from the western landfill boundary (plan and section). A 0.2 m/day velocity and 26 year "age" of the leachate plume (from 1997) is accepted. The groundwater within the Cl^- plume is anaerobic, generally methanogenic. The volume of impacted groundwater is estimated as 6.5×10^6 m^3.

Benzene, 1,2-dichloroethane (1,2-DCA), dimethyl-ketone (acetone), tetrahydrofuran (THF), 4-methyl-2-pentanone (MIBK), and isopropyl alcohol (IP) were identified in the groundwater above State residential clean-up goals. 1,1-dichloroethane (1,1-DCA), 2-butanone (MEK), 2-methyl-2-propanol (TBA) were of concern, but were found below goal concentrations. Table 1 provides some information about these chemicals and their expected groundwater velocity in a clean sand and gravel aquifer with low sorption potential (f_{OC} of 0.0006).

Golder Associates Ltd. conducted hydrogeological studies and the chemical sampling which is summarized in various reports. Ravi et al. (1998) recently developed evidence that dispersion and probably biodegradation were limiting the migration of benzene, 1,2-DCA and 1,1-DCA in the plume. In our study twenty-one locations were monitored four times (October, 1996, March 1997, July 1997, November, 1997) with the additional 4 wells included in the November, 1997 sampling. An evaluation of the collected data set indicated no strong temporal trends over the short monitoring period (Murdie, 1998).

Monitored Natural Attenuation – Current Situation and Expectations for the Future

Simply, MNA requires: that the current situation be acceptable, that it is likely that the future will also be acceptable, that a monitoring program be in place to warn if this expectation is not being met, and that some alternative action plan also be in place in that event. Where there is a high degree of confidence that the long-term situation will remain acceptable, perhaps no further action is a reasonable outcome.
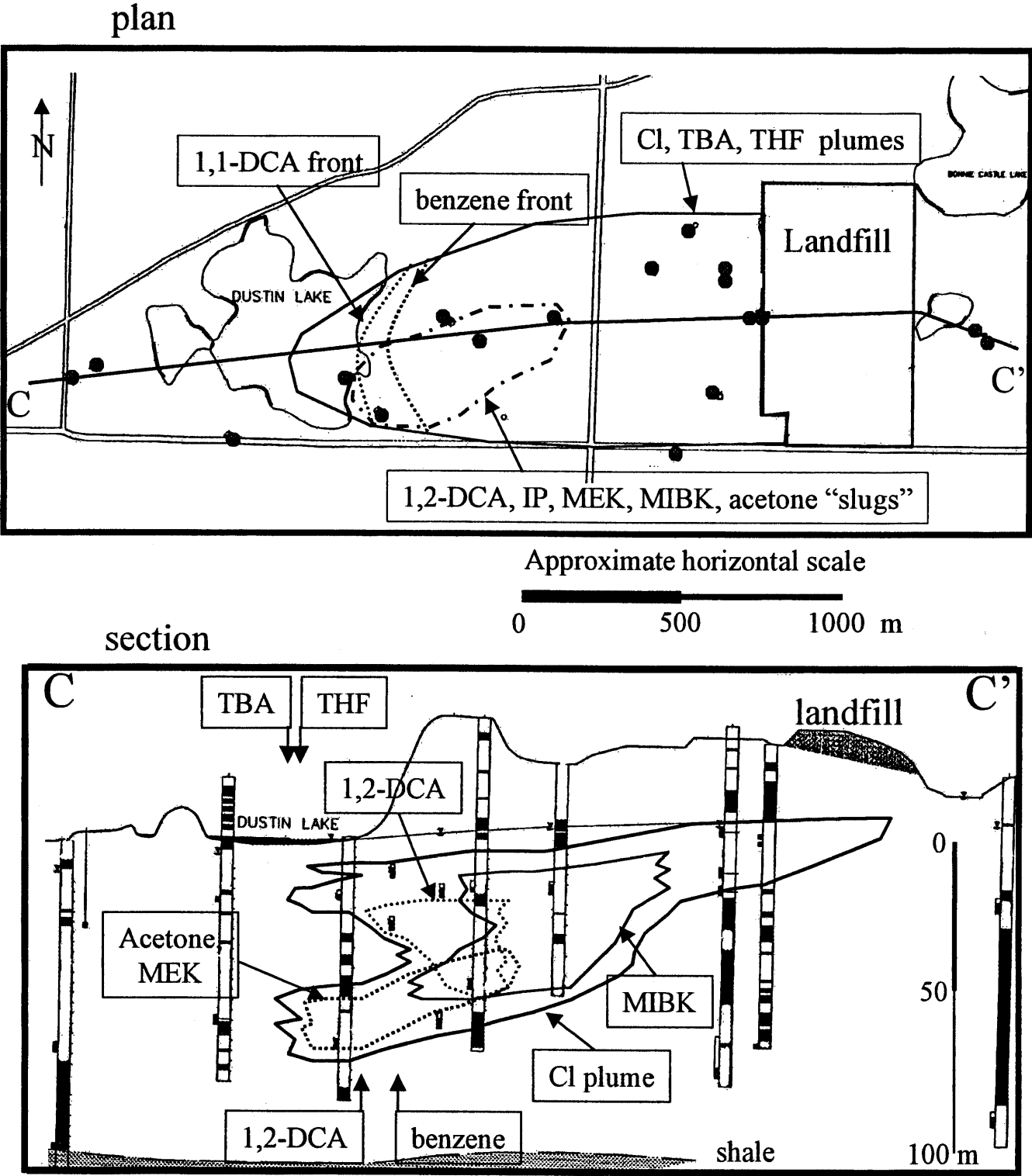
Figure 1. Plan and cross section showing the landfill, monitoring wells, basic hydrostratigraphy (dark units are aquitards), and approximate extent of the various chemical plumes.

Table 1. Chemicals of Interest

Chemical	Formula	Goal Conc. (μg/L)	Solubility* (mg/L)	K_d* #	Velocity rel. to water^	Biodegrad. Aerobic	Potential$$ Anaerobic
TBA	$(CH_3)_3COH$	3900	∞	est 0	1.0	Y	N
Benzene	C_6H_6	5	1800	0.037	0.84	Y	N
1,2-DCA	$C_2H_4Cl_2$	5	8500	0.023	0.90	N	N
1,1-DCA	$C_2H_4Cl_2$	880	5100	0.032	0.86	N	N
acetone	CH_3COCH_3	730	∞	0.0004	1.0	Y	Y
THF	C_4H_8O	240	∞	est 0	1.0	?	N
MIBK	$C_6H_{12}O$	370	19000	0.080	0.71	Y	N
MEK	C_2H_6O	13000	270000	0.0027	0.99	Y	Y
IP	C_3H_8O	470	∞	est. 0	1.0	Y	N

* : http://www.epa.gov/region09/waste/sfund/prg/s4_01.htm
\# : f_{OC} assumed as 0.0006 and K_{OC} from *; ^ : $V_{chemical}$ / V_{water} = 1 / (1 + 5K_d)
$$: based on lab microcosms using site material, Y – yes, N – none seen, ?? - slight

TBA appears to be as pervasive as Cl⁻ (see plan, Figure 1 and section, Figure 1) with attenuation mainly by dispersive dilution, but its concentrations in the plume are not currently above goal concentrations. Aerobic microcosm experiments demonstrated that TBA is aerobically transformed, so bio-attenuation in aerobic groundwater in advance of the main body of leachate should assist in limiting the extent of TBA in this aquifer.

Benzene has not advanced as far as has Cl⁻ (plan & section). This attenuation is likely due mainly to sorptive retardation of benzene (Table 1) and its initial escape from the landfill at low concentrations. Concentrations in wells located at the down gradient edge of the were considered to represent the chemical output from the landfill for 1977 to 1998. Chloride input rose from 100 to > 400 mg/L by 1981, then declined by 1984 to about 200 – 300 mg/L. Benzene, in contrast, remained at about 200 μg/L until 1986 from which time benzene concentrations ranged from 400 – 1000 μg/L. As with TBA, aerobic biotransformation was demonstrated in microcosms, so benzene may not advance significantly further into the naturally aerobic shallow aquifer.

Dispersive dilution is likely the dominant attenuation mechanism for tetrahydrofuran (THF). Very minor THF transformation was suggested in anaerobic microcosm experiments. Modeling considering only advection and dispersion suggests the THF plume was likely very close to a steady configuration and, barring unexpected increases in concentrations from the landfill, no additional groundwater should be impacted.

Very little 1,1-DCA is currently emanating from the landfill. A very dilute plume, below regulatory goal concentrations, extends at least as far as the benzene plume, suggesting that sorption and dispersion are the major attenuation mechanisms.

A number of chemicals (, 1,2-DCA, acetone, MEK, MIBK, and IP) are currently found in the leachate plume but not near the landfill. These plumes were termed "slugs" to describe this distribution and the location of these slugs is illustrated in the plan and section, Figure 1.

Acetone, MEK, and MIBK have not been found in near-landfill wells since 1993, in part, accounting for the lack of these chemicals in wells up to about 350 m down gradient of the boundary. The lack of these chemicals up to at least 600 m from the landfill boundary could reflect attenuation by dispersion and by anaerobic biotransformation. Anaerobic microcosms provided strong evidence for acetone and methyl ethyl ketone (MEK) biotransformation potential in the leachate plume, suggesting these "slugs" are declining residuals after biotransformation in the anaerobic leachate plume. Attenuation by dispersion and biotransformation appear likely to minimize advance of these plumes. Interestingly, acetone could be a biotransformation product of IP and the two chemcials do occur together in the leachate plume.

There is no near-landfill historical data for IP and no strong support for anaerobic biotransformation of IP was found in microcosms, so the reason no IP is emanating from the landfill is unclear. While aerobic biodegradation of IP may protect the down gradient shallow, aerobic aquifer, the deeper (> 50 m below the surface), anaerobic aquifer will be protected only by dispersive dilution. It may take many km before the IP "slug" reaches goal concentrations in the deeper, anaerobic segment of the aquifer. This deeper segment is not currently used for water supply, so impact of IP migration on water supply is deemed unlikely.

Methyl isobutyl ketone (MIBK) has not been found at near-landfill wells since about 1993, and so would not be expected up to perhaps 300 m down gradient of the landfill. MIBK may be significantly retarded (Table 1), restricting the advance of the front of the MIBK plume. In any event, modeling suggests dispersion will reduce concentrations to below State goals before the plume reaches under Dustin Lake and so little additional future impact is anticipated.

The "slug" of 1,2-DCA results from its decline and essential disappearance near the landfill. Neither DCA was shown to biotransform anaerobically. 1,2-DCA could travel up to about 3000 m from the landfill before dispersion will reduce concentrations below the goal concentration of 5 _g/L . However, the 1,2-DCA slug appears to be deep enough to plunge well below any down gradient shallow wells, so no impact is envisaged.

The potential for adverse impact (i.e., concentrations exceeding State goals) of the chemicals of concern on existing, down gradient groundwater supplies appears slight. It would seem that monitoring of sentry wells and residential well quality would provide adequate warning of an unexpected failure of natural attenuation.

Is MNA the Best Solution?

What are the alternatives to MNA? The Record of Decision (ROD) envisaged a pump-and-treat system near the landfill and capping the landfill to cut off future contamination. The "slugs" of 1,2-DCA and IP, which seem to present the highest risk to groundwater users, are unlikely to be remediated by such a system. However, the ROD scheme would cut off future contamination and should return the aquifer resource faster than MNA. A more extensive pumping system could remove all of the current leachate plume (6.5×10^6 m^3), even allowing that 2 to 20 times this volume will likely be removed during such clean up. Is recovery of this groundwater resource in, say, 20 to 50 years with active remediation, sufficiently better than recovery in perhaps 50 – 300 years using MNA? What is the "environmental discount rate" and how do we calculate the value of this future benefit?

The disappointing aspect of this situation is that the local public has had little direct involvement in making this value judgement. Certainly the Potentially Responsible Parties (PRPs), Federal and State authorities have roles, but what is the cost-benefit perspective of the local people? The only benefit so far has been a "free" water distribution system, providing better quality surface waters to those whose wells were impacted. Currently, these people see only costs if active remediation is undertaken - financial costs for the county and local employers (the PRPs), decreased property values associated with the perception, rather than actual impact, and bother (noise, traffic). They see little direct benefit in any remediation, other than an improvement in a resource not currently used. Surely a remedial solution should provide additional benefits to impacted individuals.

References

Murdie, L. S., 1998. Assessment of Fate and Transport of a Mixed Organic Landfill Leachate - West KL Ave. Landfill, Kalamazoo County, Michigan. M Sc Thesis, University of Waterloo, Waterloo, ON, Canada.

Ravi, V., Chen, J. S., Wilson, J. T., Johnson, J. A., Gierke, W., Murdie, L., 1998. Evaluation of Natural Attenuation of Benzene and Dichlorethanes at the KL Landfill. Bioremediation Jour., 2(3&4):239-258.

U. S. EPA Directive OSWER Directive 9200.4-17, ***http://www.epa.gov/swerust1/***d9200417.htm.

Natural Attenuation in a Landfill Leachate Plume: The Grindsted Landfill Site
(Poul L. Bjerg, Kirsten Rügge, Peter Kjeldsen, Hans-jørgen Albrechtsen, Liselotte Ludvigsen, Gorm Heron And Thomas H. Christensen, Technical University Of Denmark, Denmark)

Abstract
The Grindsted landfill site has since 1992 been subject to a major research programme at the Technical University of Denmark, focusing on a number of aspects related to natural attenuation. The main areas of interest have been (1) The interaction between the surrrounding aquifer and the landfill with respect to flow pattern and leaching of organic and inorganic landfill leachate contaminants; (2) The landfill as a source of contamination: Spatial variability in leachate composition; and (3) Natural attenuation processes in the upper part of the landfill leachate plume. The investigations of the leaching pattern showed a complex picture, where the flow field in the landfill area showed a mounding, causing pronounced spreading of the plume. Also vertical gradients were observed partly due to the mounding and partly due to very high densities of the leachate in certain areas. A pronounced spatial variability of the leachate compositions complicates the interpretation of the leaching from the landfill and may call for different remedy strategies in different areas. The natural attenuation processes have been investigated by detailed field observation studies, where the fate of organic compounds in the plume have been mapped. Also the geology, the geochemistry and in particular the redox conditions have been characterized by different methods (e.g. redox sensitive species, microbial assays, hydrogen measurements). A rapid disappearence of the organic compounds indicated a substantial natural attenuation of mainly BTEX compounds in the anaerobic part of the plume; however, no direct evidence could be provided. As a consequence a number of different degradation experiments have been carried out: laboratory batch experiments, in situ microcosm and continous, natural-gradient injection experiments in the anaerobic part of the plume. This paper outlines some of the main results from these experiments and discusses the general aspects of natural attenuation of landfill sites based on the Grindsted landfill case.

1.   Introduction

The xenobiotic compounds benzene, toluene, ethylbenzene, and xylenes (BTEX) as well as different types of chlorinated aliphatic compounds are often found in groundwater affected by landfill leachate (Christensen et al., 1994). These compounds constitute a serious problem for groundwater pollution due to their potential health risk. A large number of old landfills exist through out the world, and traditional remedial action (excavation, capping, pump- and treat) is not realistic at all these sites. This makes natural attenuation or intrinsic remediation very interesting as a remediation strategy 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 paper was to provide an overview of the field observation and experiments performed at the Grindsted landfill in the period from 1992 to 1998. The field studies relate to different aspects of natural attenuation in the leachate plume, and also some of the features of the source at the landfill site. The information is used as a background for discussing the application of natural attenuation at landfill sites in general.

2.   The Grindsted Landfill Site

2.1   The Source

The Grindsted landfill site in Denmark has been subject to a number of investigations since 1992. The site is located in the western part of Denmark and placed on top of the original surface (Figure 1). Disposal of waste took place between 1930 and 1977, and approximately 300,000 tonnes of waste have been deposited, mainly between 1960 and 1970 (Kjeldsen et al., 1998a).

The waste consists of: Municipal solid waste (20%); bulky waste, garden waste and street waste (5%); industrial waste (20%); sewage treatment sludge (30%); and demolition waste (25%). The spatial variability of the leachate quality was investigated by sampling (31 wells) below the landfill in the uppermost groundwater (a small unsaturated zone exists beneath the landfill). The results revealed a significant spatial variability in the leachate composition and the landfill could be divided into four main areas (Figure 2.). The average concentrations in the strong leachatewere typically 20-40 times higher than in the weak leacahte with respect to concentrations of ammonium, chloride and dissolved organic carbon (DOC). The strong leachate was located in the northern part of the landfill and originated from dumping of industrial waste. The large heterogeneities in the leachate quality may generate multiple plumes with different properties and call for differentiated remedial actions, mainly directed towards the industrial hot spot area.
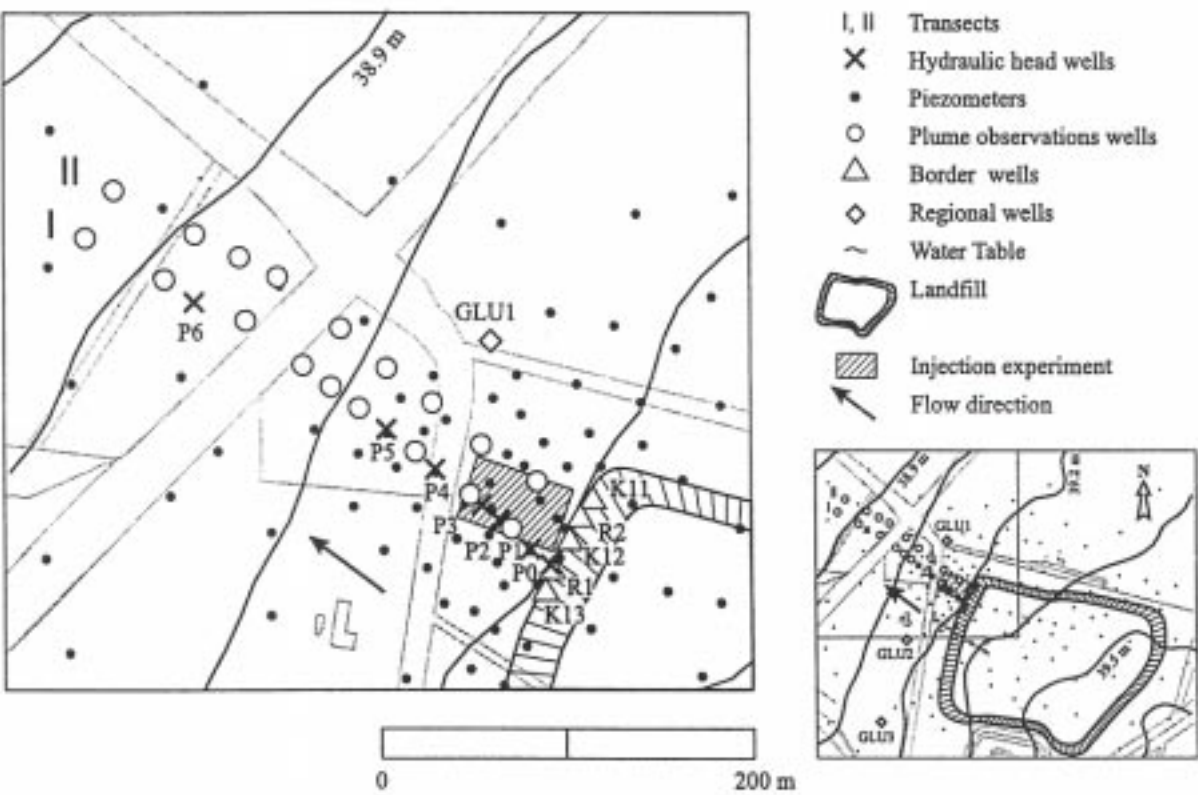
Figure 1.   Location of the Grindsted landfill site, overview of wells and investigated transects.
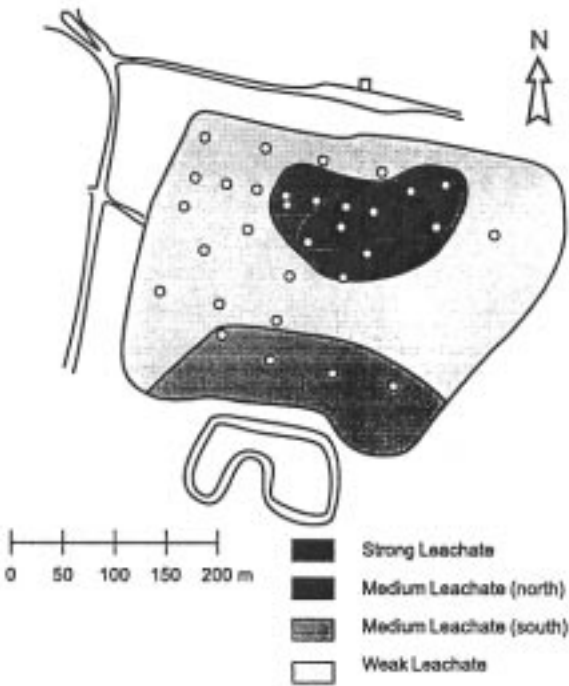

Figure 2.   Division of the landfill into four areas with different leachate (Kjeldsen et al., 1998a).

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2.2   *Geology and Hydrogeology*

The Grindsted Landfill is located on a glacial outwash plain. The upper 10-12 m of the unconfined aquifer consists of an upper Quaternary sandy layer and a lower Tertiary sandy layer, locally separated by discontinuous silt and clay layers (Heron et al., 1998). Investigations of the hydraulic conductivity and hydralic gradients resulted in pore flow velocities of approximately 50 and 10 m/year for the Quaternary and Tertiary sandy layers, respectively. A clay layer of approximately 1 m thickness located 12 m below ground surface extends over a large area of the landfill. Below this layer is a more regional Micaceous sandy layer of approximately 65 m thickness. This layer is vertically delimited by another low-permeable clay layer approximately 80 m below ground surface.

The groundwater overall flow is northwesterly, but the isopotential contours are semicircular, indicating a diverging flow. Locally, inside and close to the landfill, the flow field shows significant seasonal variation (Figure 3). The reasons for this mounding have not been fully understood, but Kjeldsen et al (1998) suggested three possibilities: (1) higher infiltration in this part of the plume; (2) lower hydraulic conductivity in the aquifer underlying this part of the landfill e.g. due to differences in geology, bacterial growth, precipitates or gaseous bubbles of methane and carbondioxide; or (3) higher infiltration in the borders of the mounding area. This local mounding results in enhanced lateral spreading of the plume, but also downward directed hydraulic gradients in the groundwater below the landfill. The latter can cause an unexpected vertical spreading pattern, while the enhanced spreading affects the dilution of the plume. The seasonal variations in the flow field are important for the design of monitoring networks and interpretation of time series of monitoring data.
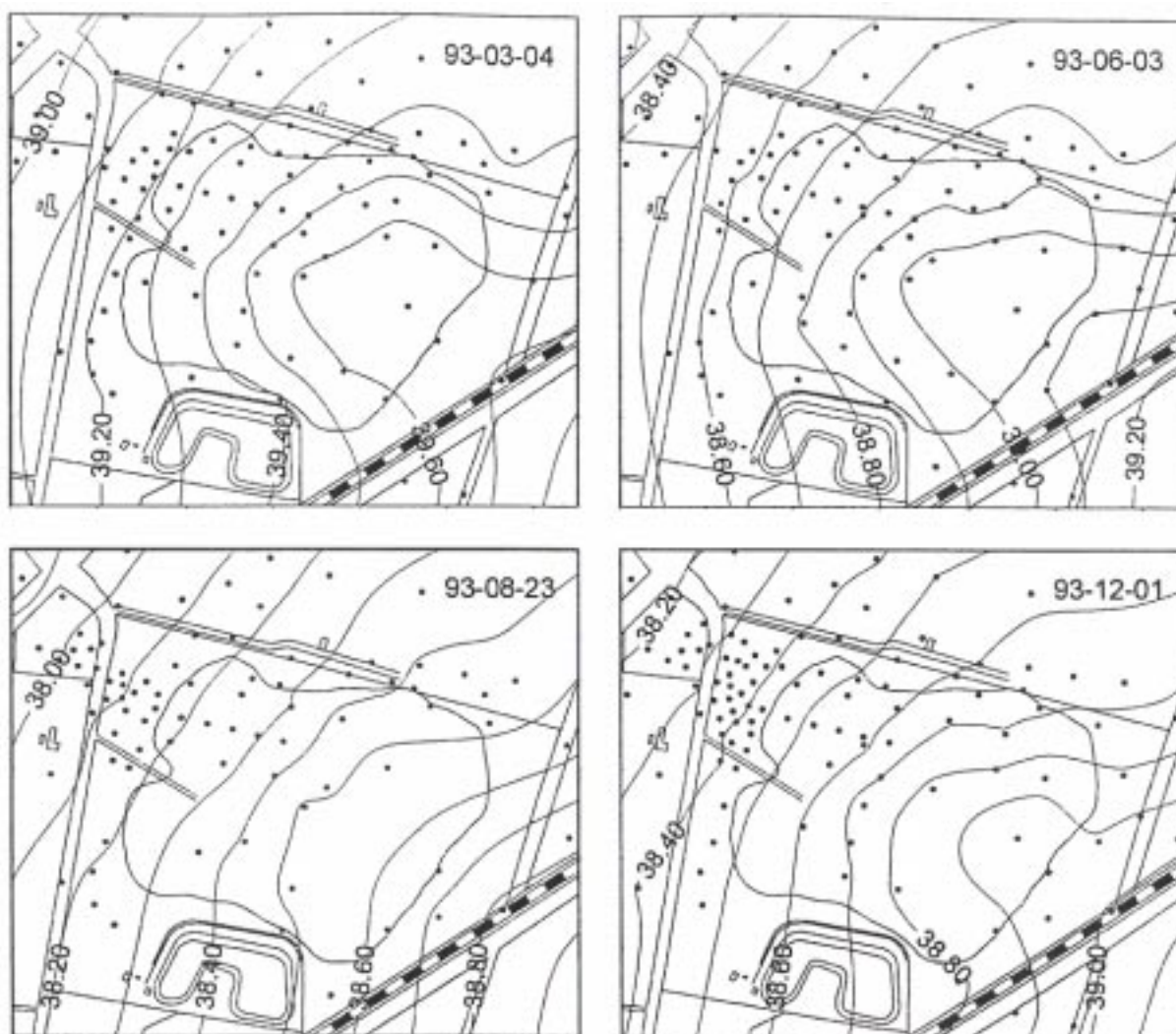

Figure 3.   Mounding of the leachate-groundwater table below Grindsted Landill shown as isopotential contours for the landfill and surrounding area at 4 different seasons during 1993. Modified from Kjeldsen et al. (1998).

2.3   Landfill Leachate Plume

The investigations of the landfill leachate plume at the Grindsted landfill have been restricted to the upper aquifer (10-12 m) in two transects starting at the western border of the landfill. Transect I (Figure 1) has been characterized in great detail with respect to:

- Geology and hydrogeology (Bjerg et al., 1995; Heron et al., 1998; Petersen et al., 1999b)

- Inorganic and /or redox sensitive compounds (Bjerg et al., 1995)

- Hydrogen levels and in situ energetics (Bjerg et al., 1997; Jakobsen et al., 1998);

- Aquifer solid composition (Heron et al., 1998)

- Microbiology and microbial redox processes (Ludvigsen et al. , 1997, 1998,1999)

- Distribution of xenobiotic organic compounds (Rügge et al., 1995; Holm et al., 1995)

- Toxicity related to xenobiotic organic compounds (Baun et al., 1999)

- Modelling of natural attenuation processes (Petersen et al, 1999a,b)

The information gathered on redox conditions and fate of organic compounds will briefly be summarized here. Redox characterization based on the distribution of redox sensitive species is presented in Figure 4. At the border of the landfill and within a distance of 50 m from the landfill, methanogenesis and sulfide reducing conditions occur (Bjerg et al., 1995). Iron reducing conditions dominate 50-85 m from the landfill, and from 85 m manganese is the primary e-acceptor. Further away nitrate reducing conditions are prevalent and finally the aquifer becomes aerobic. The redox zonation suggests that several redox zones overlap in the anaerobic part of the plume. This was confirmed by bioassays (microbially active, unamended incubations of aquifer material and groundwater) monitoring the relevant redox processes (Ludvigsen et al., 1998). The bioassays showed that more than one redox process was significant in several samples; however, in most cases one electron acceptor dominated in terms of equivalent turnover of organic carbon. Elaborated use of the hydrogen concentrations also suggest that microbial redox processes take place simultaneously. Overall the Grindsted landfill leachate plume along this transect hosts a complex picture of anaerobic redox processes within a distance of 250 m from the landfill border, where aerobic conditions are established again. The investigations of the redox conditions at the Grindsted site suggest, that the redox sensitive compounds may be a good indication of redox conditions, but for detailed characterization of the actual redox processes an array of methods must be applied.

The distribution of xenobiotic compounds was also mapped in Transect I (Figure 4). More than 15 different organic compounds were identified close to the landfill. The BTEX compounds dominated with concentrations of 0-222 µg/L close to the landfill, and a single observation of *o*-xylene concentrations up to 1550 µg/L (Rügge et al., 1995). No chlorinated aliphatic compounds were found in this part of the pollution plume. Most of the xenobiotic organic compounds were no longer detectable approximately 60 m from the edge of the landfill site. Since dilution and sorption could not account for the disappearance of the xenobiotic compounds, it was proposed that the majority of the xenobiotic compounds in the leachate were transformed under methanogenic/sulfate-reducing or iron-reducing conditions in the aquifer. It should be emphasized that the apparent attenuation close to the landfill was not based on a direct proof, but on a comparison of the leaching period, dilution and sorption in the plume to the actual distribtion. This was for a number of compounds convincing, and also supported by reactive solute transport modelling. However, benzene shows a distribution that can indicate recalcitrance in the most reduced parts of the plume, but fast disappearance in more oxidized enviroments (see e.g. discussion on benzene in Petersen et al., 1999b). Final conclusions based on field observations may therefore be a difficult task, and building up solid information may involve a large amount of data within different disciplines.

2.4   Evidence for Natural Attenuation of Xenobiotic Compounds

The degradation of xenobiotic compounds can Besides field observations as presented above, the degradation of xenobiotic compounds can be investigated by microcosm/column experiments and field injections experiments. At the Grindsted site the degradation of a mixture of xenobiotic compounds (seven aromatic hydrocarbons, four chlorinated aliphatic hydrocarbons, five nitroaromatic hydrocarbons, two pesticides) was studied using *in situ* microcoms (ISM) and laboratory microcosm (LM) (Bjerg et al., 1999; Rügge et al., 1998, 1999a,b). The data from degradation experiments were compared to the field observation data of the aromatic hydrocarbons and we will limit the discussion to these compounds.

In the anaerobic field injection experiment, an anaerobic stock solution of the xenobiotic compounds was injected along with bromide as tracer into five injection wells, installed 15 m downgradient of the landfill. The amount of water
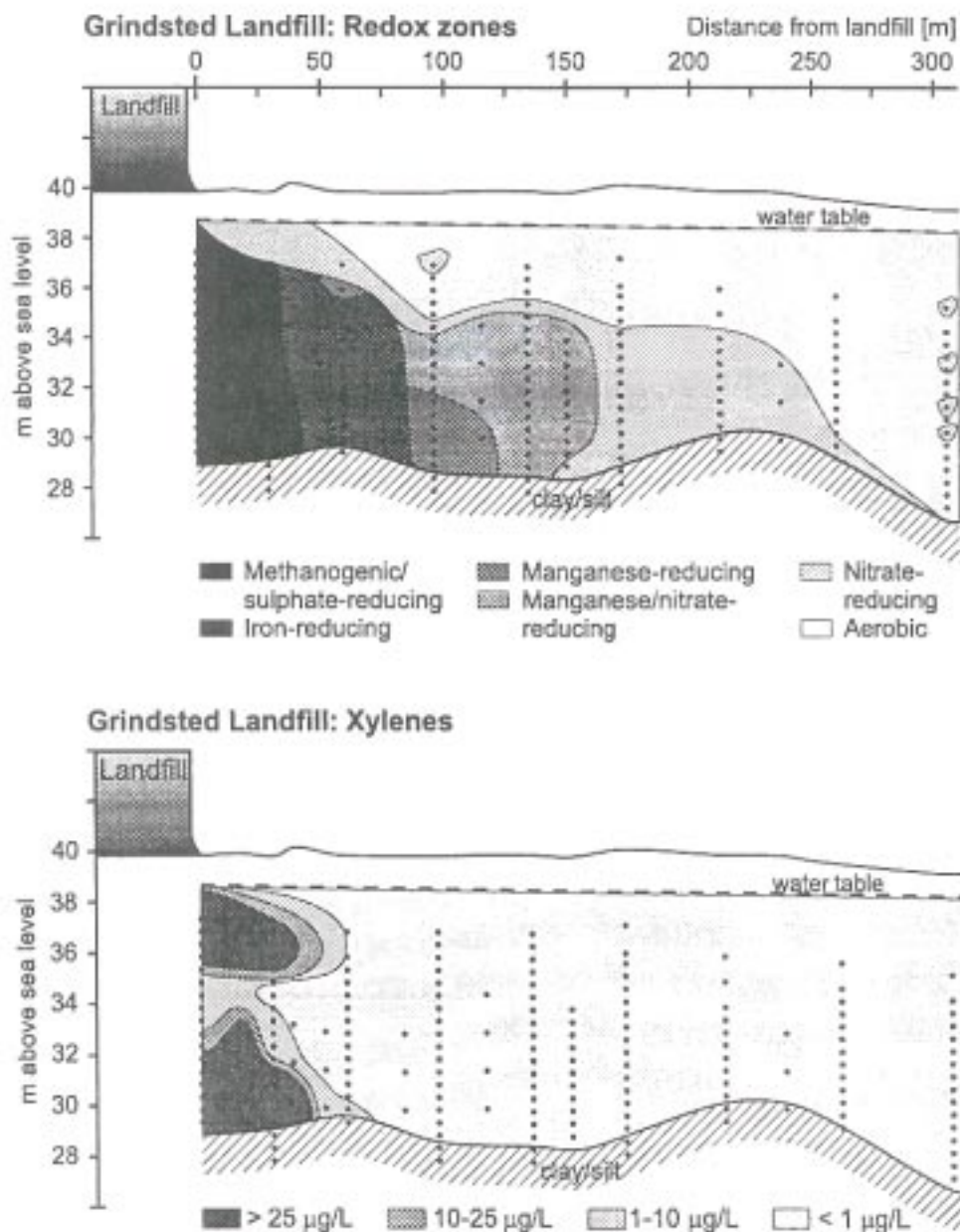
Figure 4. Proposed redox zonation, and distribution of xylenes in Transect I at the Grindsted Landfill (From Bjerg et al., 1995 and Rügge et al. 1995).

injected in the natural gradient experiment was approximately 5% of the groundwater flux passing the injection wells, yielding approximate concentrations of 75-330 μg 1^{-1} of the xenobiotic compounds and 100 mg 1^{-1} bromide 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). Over a period of 924 days samples were collected from approximately 70 discrete sampling points in the central part of the cloud (the injected plume)for the determination of breakthrough curves. From these curves 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. 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. This was supplemented by groundwater and sediment charac- terizations and microbial assays conducted on sediment and groundwater sampled 800 days after start of the injection (Albrechtsen et al., 1999).

In the injection experiment, degradation was observed as a complete mass removal of toluene, within the most re- duced part of the aquifer where iron reduction, sulfate reduction and methanogenesis occurred. Partial degradation was observed for *o*-xylene. The degradation of *o*-xylene was not initiated before the cloud had reached the less reduced part of the aquifer. Examples of the cloud observations after 649 days are given in Figure 5. Benzene was not degraded within the experimental period of 924 days. Due to highly varying background concentrations it was not possible to determine whether any degradation of the compounds ethylbenzene and *m/p*-xylene occurred.

In parallel to the injection experiment, *in situ* microcosms (ISMs) were installed at five locations downgradient of the landfill (see Nielsen et al., 1996 for description of this technique). Also laboratory batch experiments (LBs) were con- ducted with sediment and groundwater from the corresponding locations. The experimental periods of the 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., 1999). For the aromatic compounds only toluene was degraded in the ISM, while *o*- and *m/p*-xylenewere degraded in the LB. Benzene, ethylbenzene and naphthalene were not degraded in either the ISM or the LB.
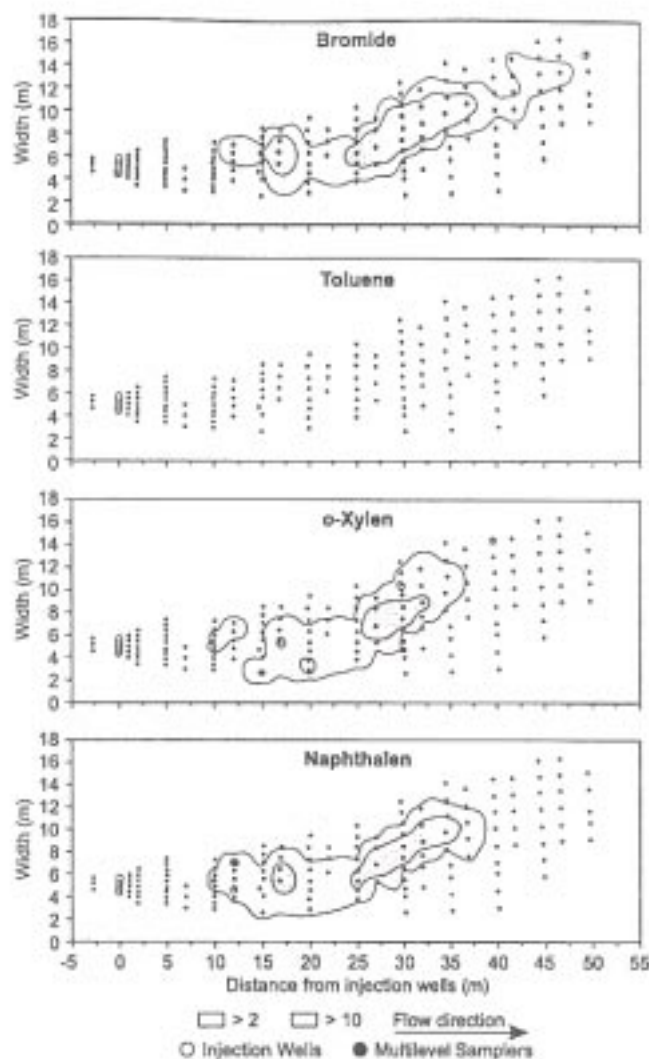

Figure 5.   Observed clouds of bromide, toluene, o-xylene, naphthalene after 649 days. Bromide in g/m^2, xenobiotics in mg/m^2 (From Rügge et al., 1999a).

10

In general a good accordance was observed between the results obtained in the injection experiment, the ISMs, and the LBs; however, a few differences can be noticed, as shown in Table 1. These differences were mainly due to the different experimental periods, namely 924 days in the injection experiment, and up to 210 and 537 days in the ISMs and LBs, respectively. However, 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 with lag periods shorter than 50-100 days. LBs are also a useful and cost-saving approach for studying degradation. As the batch set-up allows for very long experimental periods, 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 (BTEX and napthalene), and it is not known how well the batch experiments mimic the field situation for more complex compounds.

The experiments carried out in the anaerobic part of the leachate plume support that natural attenuation of toluene and o-xylene takes place close to the landfill. However, the results for ethylbenzene are not in accordance with the plume observations. In the case of benzene the degradation may take place in a longer distance from the landfill in more oxidized environments (see Petersen et al., 1999b).

All together, establishment of evidence for natural attenuation is not an easy task and may involve different approaches including field observations, experiments in laboratory and field, and also reactive solute transport modelling. The latter is an important tool for integration of data on geology and hydrogeology, redox conditions, distribution of xenobiotic compounds and degradability/ degradation rates.

3.   Implications for Natural Attenuation

The results from the Grindsted landfill site presented here, previous data from the Vejen landfill site (Lyngkilde and Christensen, 1992a,b), and recent data from KL landfill (Ravi et al., 1998) indicate a significant potential for natural attenuation at landfills sites with respect to xenobiotic organic compounds. These are, however, only a few examples, compared to the number of landfill sites around the world and therefore more well-documented examples are necessary. Experience from new sites will also help in developing procedures for demonstration of natural attenuation, but such a database of examples cannot solve the problems that may complicate a widespread use of natural attenuation as a remediation strategy at landfill sites. Currently, based on the experience presented in this paper and the general obstacles reviewed by Christensen et al. (1999), five points will be critical:

- Local hydrogeological conditions in the landfill area may affect the spreading of the contaminants

- The size of the landfill and the heterogeneity of the source may create a variable leaching pattern and maybe also multiple plumes

- The complexity of leachate plumes with respect to compounds (inorganic, xenobiotic organic compounds and bio-geochemical processes)

Table 1.   Potential for Degradation of the Aromatic Compounds in Anaerobic Leachate Affected Groundwater

	benzene	toluene	ethyl-benzene	m/p-xylene	o-xylene	naphthalene
Grindsted Landfill						
(1) Field Injection 15-45 m	-	+	?	?	-	-
(1) Field Injection 45-65 m	-	+	?	?	+	-
(2) ISM and LB						
LB (I) 15	-	+	-	-	-	-
LB (II) 15	-	+	-	-	-	-
LB (II) 25	-	+	-	-	-	-
ISM 25	-	-	-	-	-	-
LB (II) 35	-	-	-	-	-	-
ISM 35	-	-	-	-	-	-
LB (II) 45	-	-	+	-	-	-
ISM 45	-	-	-	-	-	-
LB (II) 55	-	-	+	+	-	-
ISM 55	+	-	-	-	-	-
LB (I) 60	-	+	-	+	+	-

+ degradation observed
- no degradation observed
? not possible to determine due to highly varying background conditions
(1) Rügge et al. (1999a), (2) Bjerg et al. (1999)

- The time frame for leaching from a landfill site will be very long and calls for long-term evaluation of the attenuation capacity

- Demonstration of natural attenuation in terms of mass reduction at the field scale

The importance of each issue will depend on the actual landfill. It should be emphasized that even though these problems may be difficult to solve, very few alternatives exist for remediation at landfill sites and none of these alternatives, e.g. excavation, capping and pump-and-treat, do in reality solve the problems (Christensen et al., 1999).

4.   Conclusion

The application of natural attenuation as a remediation strategy at landfill sites may be an attractive approach; however, the complexity of landfill as a source and the biogeochemistry of landfill leachate plumes suggest that it will be difficult to develop a simple routine approach. At the moment, it will be useful to build up a comprehensive database on actual landfill plumes and focus the activities on demonstration projects in different countries in order to develop useful protocols. The projects should be made in a cooperation among researchers in the area, consulting companies and the authorities.

5.   List of References

Albrechtsen, H.-J., Bjerg, P.L., Ludvigsen, L., Rügge, K. & Christensen, T.H. (1999): An anaerobic field injection experiment in a landfill leachate plume (Grindsted, Denmark), 2. Deduction of anaerobic (methanogenic, sulfate- and Fe(III)-reducing) redox conditions. Accepted for publication in *Water Resources Research*.

Baun, A.; Kløft, L.; Bjerg, P.L.; Nyholm, N. (1998): Toxicity testing of organic chemicals in groundwater polluted with landfill leachate. Accepted for publication in *Environmental Toxicology and Chemistry*.

Baun, A.; Jensen, S.D., Bjerg, P.L., Christensen, T.H.; Nyholm (1999): Toxicity of organic chemical pollution in groundwater downgradient of a landfill (Grindsted, Denmark). Submitted for publication in *Environmental Science and Technology*.

Bjerg, P.L., Jakobsen, R., Bay, H., Rasmussen, M., Albrechtsen, H.-J. & Christensen, T.H. (1997): Effects of sampling well construction on H2 measurements made for characterization of redox conditions in a contaminated aquifer. *Environmental Science and Technology*, **31**, 3029-3031.

Bjerg, P.L., Rügge, K., Cortsen, J., Nielsen, P.H. & Christensen, T.H. (1999): Degradation of aromatic and chlorinated aliphatic hydrocarbons in the anaerobic part of the Grindsted Landfill leachate plume: In situ microcosm and laboratory batch experiments. *Ground Water,* **37** (1) , 113-121.

Bjerg, P.L., Rügge, K., Pedersen, J.K. & Christensen, T.H. (1995): Distribution of redox sensitive groundwater quality parameters downgradient of a landfill (Grindsted, Denmark). *Environmental Science and Technology*, **29**, 1387-1394.

Christensen, T.H.; Bjerg, P.L. & Kjeldsen, P. (1999): Natural attenuation : A feasible approach to remediation of groundwater pollution at landfill. Submitted for publication in Groundwater Monitorng and Remediation

Heron, G., Bjerg, P.L., Gravesen, P., Ludvigsen, L. & Christensen, T.H. (1998): Geology and sediment geochemistry of a landfill leachate contaminated aquifer (Grindsted, Denmark). *Journal of Contaminant Hydrology*, **29**, 301-317.

Holm, J.V., Rügge, K., Bjerg, P.L. & Christensen, T.H. (1995): Occurrence and distribution of pharmaceutical organic compounds in the groundwater downgradient of a landfill (Grindsted, Denmark). *Environmental Science and Technology*, **29**, 1415-1420.

Jensen, D.L., Boddum, J.K., Redemann, S. & Christensen, T.H. (1998): Speciation of dissolved iron(II) and manganese(II) in a groundwater pollution plume. *Environmental Science and Technology*, **32**, 2657-2664.

Kjeldsen, P. & Skov, B. (1994): A simple method for measuring the verticality of small driven wells. *Ground Water Monitoring and Remediation*, **9**, (3), 107-110.

Kjeldsen, P., Bjerg, P.L., Rügge, K., Christensen, T.H. & Pedersen, J.K. (1998a): Characterization of an old municipal landfill (Grindsted, Denmark) as a groundwater pollution source: Landfill hydrology and leachate migration. *Waste Management and Research*, **16**, (1), 14-22.

Kjeldsen, P., Grundtvig, Aa., Winther, P. & Andersen, J.S. (1998b): Characterization of an old municipal landfill (Grindsted, Denmark) as a groundwater pollution source: Landfill history and leachate compostition. *Waste Management and Research*, **16**, (1), 3-13.

Ludvigsen, L., Albrechtsen, H.-J., Heron, G., Bjerg, P.L. & Christensen, T.H. (1998): Anaerobic microbial redox processes in a landfill leachate contaminated aquifer (Grindsted, Denmark). *Journal of Contaminant Hydrology*, **33**, 273-291.

Ludvigsen, L., Albrechtsen, H.-J., Holst, H. & Christensen, T.H. (1997): Correlating phospholipid fatty acids (PLFA) in a landfill leachate polluted aquifer with biogeochemical factors by multivariate statistical methods. *FEMS Microbiology Reviews*, **20**, 447-460.

Ludvigsen, L., Albrechtsen, H.-J., Ringelberg, D., Ekelund, F. & Christensen, T.H. (1999): Microbial distribution and composition in a landfill leachate contaminated aquifer (Grindsted, Denmark). Accepted for publication in *Microbial Ecology*.

Lyngkilde, J. & Christensen, T.H. (1992a): Fate of organic contaminants in the redox zones of a landfill leachate pollution plume (Vejen, Denmark). *Journal of Contaminant Hydrology*, **10**, 291-307.

Lyngkilde, J. & Christensen, T.H. (1992b): Redox zones of a landfill leachate pollution plume (Vejen, Denmark). *Journal of Contaminant Hydrology*, **10**, 273-289.

Nielsen, P.H., Christensen, T.H., Albrechtsen, H.-J. & Gillham, R.W. (1996): Performance of the in situ microcosm technique for measuring the degradation of organic chemicals in aquifers. *Ground Water Monitoring and Remediation*, **16**, (1), 130-140.

Petersen , M.J.; Engesgaard, P.; Rügge, K.; Bjerg, P.L. (1999a). Modeling of natural attenuation, 1. Reactive transport in a field injection experiment in the anaerobic part of a landfill plume. Submitted for publication in Water Resources Research.

Petersen , M.J.; Engesgaard, P.; Rosbjerg, D.; Bjerg, P.L. (1999b). Modeling of natural attenuation, 2. Large scale reactive transport in a landfill plume. Submitted for publication in Water Resources Research

Ravi, V., Chen, J.S., Wilson, J.T., Johnson, J.A., Gierke, W., Murdie, L. (1998). Evaluation of natural attenuation of benzene and dichloroethane at the KL Landfill, **2**, *Bioremediation Journal*, 239-258.

Rügge, K., Bjerg, P.L. & Christensen, T.H. (1995): Distribution of organic compounds from municipal solid waste in the groundwater downgradient of a landfill (Grindsted, Denmark). *Environmental Science and Technology*, **29**, 1395-1400.

Rügge, K., Bjerg, P.L., Mosbæk, H. & Christensen, T.H. (1999a): Fate of MCPP and atrazine in an anaerobic landfill leachate plume (Grindsted, Denmark). Accepted for publication in *Water Research*.

Rügge, K., Bjerg, P.L., Pedersen, J.K., Mosbæk, H. & Christensen, T.H. (1999b): An anaerobic field injection experiment in a landfill leachate plume (Grindsted, Denmark), 1. Experimental set-up, tracer movement and fate of aromatic and chlorinated compounds. Accepted for publication in *Water Resources Research*.

Rügge, K., Hofstetter, T.B., Haderlein, S.B., Bjerg, P.L., Knudsen, S., Zraunig, C., Mosbæk, H. & Christensen, T.H. (1998): Characterization of predominant reductants in an anaerobic leachate-affected aquifer by nitroaromatic probe compounds. *Environmental Science and Technology*, **32**, 23-31.

Monitored Natural Attenuation as a Remediation Tool for an Industrial Site

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Abstract

Intrinsic Bioremediation of dissolved petroleum hydrocarbons released from a virgin naphtha contaminated site has been evaluated in a storage tank facility located in northern Italy, where approximately 600 m^3 of virgin naphtha was spilled.

A dual-pump extraction system (installed in three pumping wells) allowed the recovery of the floating phase; however, this installed hydraulic barrier capture zone did not reduce the dissolved plume expansion.

This study verifies the capacity of the phreatic aquifer to reduce the concentrations in the groundwater below the regulatory standards monitored in each point of compliance installed close to the property boundary.

A site characterization has been carried out in order to achieve complete knowledge of the site-specific geologic and hydrogeologic data required to define a conceptual understanding of groundwater flow, plume location, plume direction, contaminant concentration and attenuation over time and distance. Microbial enumeration provided evidence that the microorganism hydrocarbons degraders were present.

Shallow monitoring wells were installed along the groundwater flow pathways and were sampled for intrinsic remediation parameters. The monitoring activities have been carried out quarterly.

The results indicate that the groundwater contamination is attenuated to acceptable standards within 150 m from the source area, and that the plume is stable.

Introduction

In July 1996, in northern Italy, the leaking of an above ground storage tank (called S16 - Figure 1), located in a hydrocarbon deposit facility, led to the spilling of roughly 600 m^3 of virgin naphthathat seeped and contaminated the soil located directly below the storage tank. The product infiltrated the relatively highly permeable soil reaching the phreatic aquifer which, at the time, was roughly 7-8 meters below ground level. The direction of the latter is S/SW.

At the location of the spill the presence of a clayey silt lens roughly 1.5 m thick at an average depth of -13 m bs has been demonstrated. This lens was found at PZ11, PZ18, PZ3, PZ15, PZ19, PZ17, PZ8 and PZ22. The subsurface soil at the location is mainly comprised of alluvial deposits of medium to fine sands, which seem to be fairly homogeneous.

The main hydrogeologic parameters of the aquifer are given in Table 1.

Emergency Phase Remedial Action

In order to address the problem of the free phase product present, a hydraulic barrier consisting of 3 wells (ø 400 mm) having a depth of 25 m was setup. Each well was equipped with a dual phase pump system, which allows the recovery of the floating product. The recovered naphtha is stocked in a temporary storage tank and is periodically pumped in an above ground storage tank.

The extracted water is sent to a stripping tower able to separate the hydrocarbon's dissolved phase. The water is then discharged in a nearby river with respect to specific Italian target levels for hydrocarbons.

Monitoring

In order to verify the efficiency of the hydraulic barrier and the expansion of the dissolved phase, a network of monitoring wells, and multi-depth probes for assessing soil gas were installed.

Soil Gas Survey

To extend the information relevant to the state of subsurface contamination, a total of 13 multiple-level soil gas probes were installed at depths of -2.5 and -5 meters below ground level. Probes have a micro-screened section of PVC, 50 cm
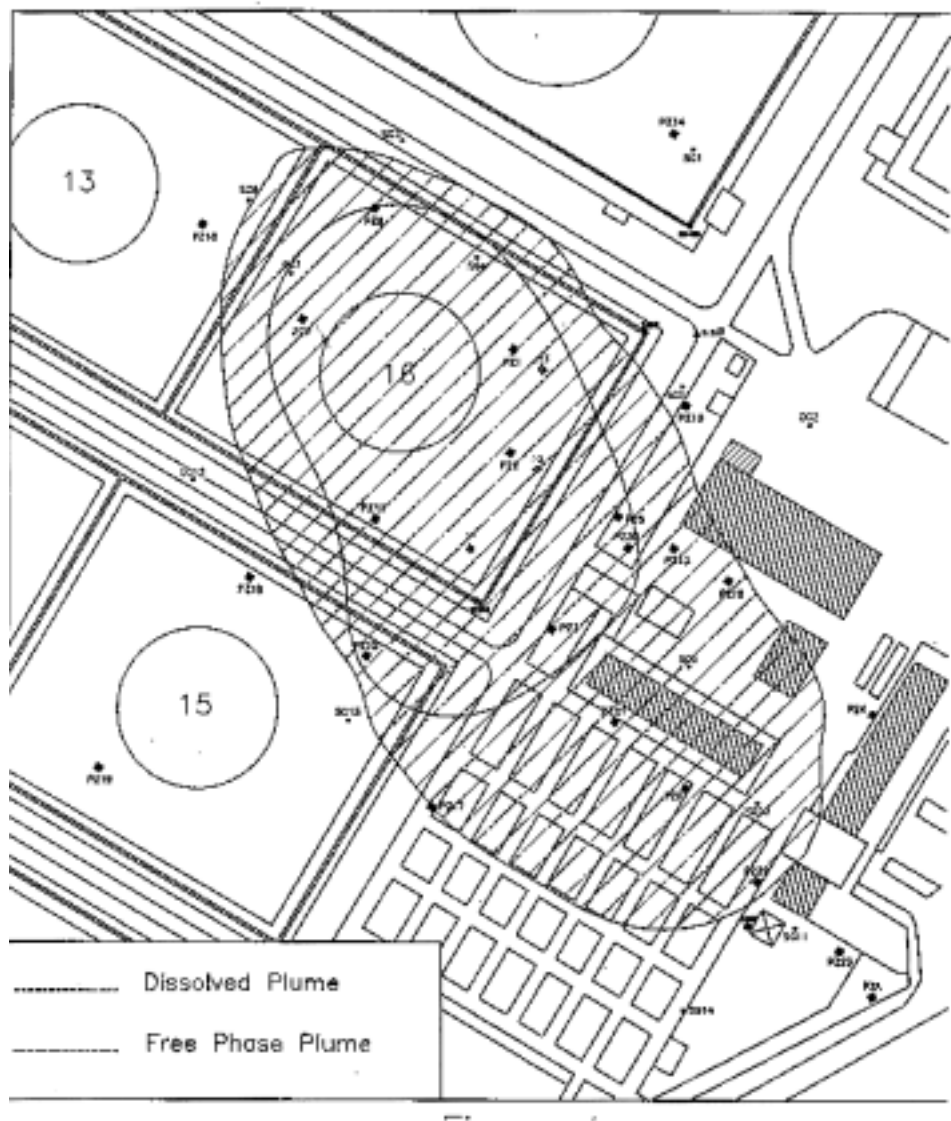
Figure 1. Map of the contaminated site. Indicated are the dimensions of the floating free product and the plume extensions.

Table 1. The Hydrological Characteristics of the Aquifer at the Location

Hydraulic gradient	$2.5 * 10^{-3}$
Mean transmissivity	$2 * 10^{-2}$ m^2/sec
Mean storage coefficient	0.2
Mean hydraulic conductivity	$5 * 10^{-3}$ m/sec

The area surrounding the storage facility is mainly characterized by rice cultivation that due to the high quantity of water used for irrigation, causes groundwater fluctuations of up to 3 m. Historical data on fluctuations showed groundwater levels were generally lowest in March and highest in September.

in length. The probes were installed for the monitoring of VOCs present in the vadose zone. The instrumentation used for the analyses was a portable PID (Photo ionizing detector) by HNU® which expresses all VOCs to benzene and a Draeger® Field instrument for the monitoring of O_2 and CO_2 (Figure 2). From the isoconcentrations it could be seen that the quantity of oxygen is proportional to the quantity of CO_2.

Monitoring Wells Location and Groundwater Sampling

In three successive monitoring campaigns (phased approach), a total of 24 wells was installed (PZA and PZ1-PZ23) in accordance to AGI (*Italian Geotechnical Association*). Each well has a diameter of 3" and has an average screened section of 4-6 m due to the GW seasonal fluctuations. Only PZ13 was screened between -12.50 and -14.50 to monitor the underlying aquifer, which has been shown to be uncontaminated. Along the centerline of the contaminant, a total of 8 monitoring wells (PZ16, PZ7, PZ3, PZ21, PZ8, PZ22, PZ23, and PZA) are present.

Groundwater samples were taken between July 1996 and March 1998. All sampling procedures were in accordance to ASTM and EPA standards. The following parameters were measured directly in the field: DO, pH, ORP, conductivity and temperature. Water samples were sent to our laboratory and analyzed for TPH, BTEX, PAH and TMB, NO_3, NO_2 NH_3, SO_4, Fe^{2+}, Fe^{3+}, Mn, CH_4, alkalinity, total phosphorus.

The frequency of the monitoring campaign was on a quarterly basis. This allowed us to collect the necessary data in order to better define the spatial distribution of the electron acceptors and metabolic byproducts both within the hot spot boundary and outside.

It is important to underline that the recovery of the free phase product by the extraction wells has obviously influenced in a substantial way the downflow of the groundwater hindering and limiting the further expansion of the plume. Therefore, when interpreting the data, it is necessary to take into account the effects of the hydraulic barrier made up by the extraction well network setup within the hotspot.

Groundwater Chemistry

The first line of evidence of Natural Attenuation processes is represented by the variation of the concentrations of contaminants versus time.
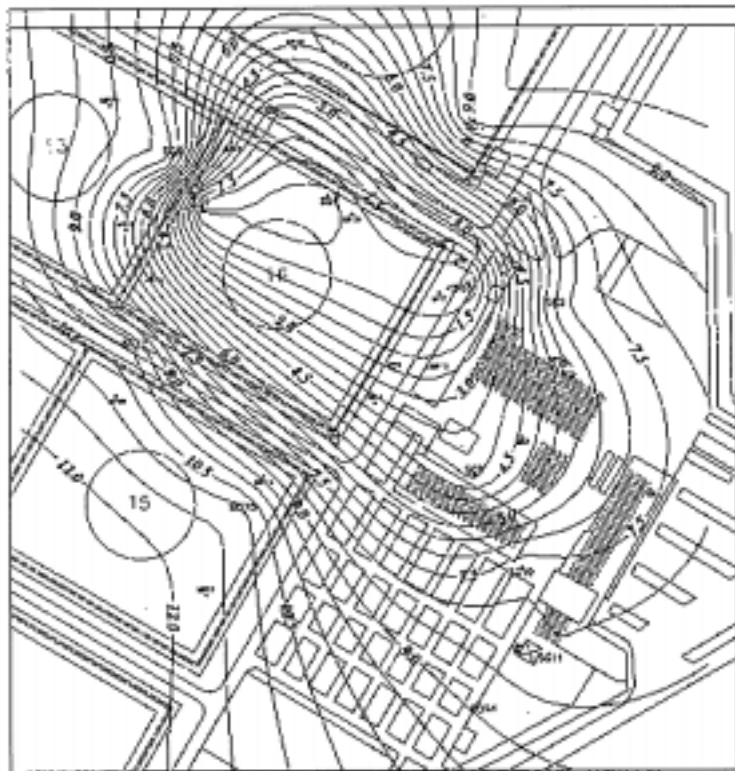

Figure 2.   The oxygen concentrations in the unsaturated zone in volume-%.

Figure 3 illustrates the absence of variation of Total Dissolved Hydrocarbons distribution in the period September '96tp March '98. Hence it is possible to assume that the plume is stable. This hypothesis will be accurately verified during the next monitoring campaigns.

The second line of evidence for NA processes is a documented loss of contaminant mass by chemical and geochemical data. In this respect, accurate evaluations were carried out to assess the aerial distribution of the main electron acceptors and other indicators of NA processes.

The oxidation/reduction potential (ORP) varies between 190 mV in aerobic environments, to negative values in correspondence of the more highly contaminated monitoring characterized by strictly anaerobic conditions. As a matter of fact, it could be noted that there is a decreasing concentration of dissolved oxygen along the plume (0.2 mg/l) compared to background values (4-6 mg/l) (Figure 4). By comparing other analytical data, it is possible to note that the nitrate concentrations diminish coherently in time with the utilization of sulfates normally present in a more reduced environment.

More reduced metabolic byproducts such as methane have never been detected throughout the site. Microbiological characterizations performed in laboratory confirm the observations described by geochemical parameters.
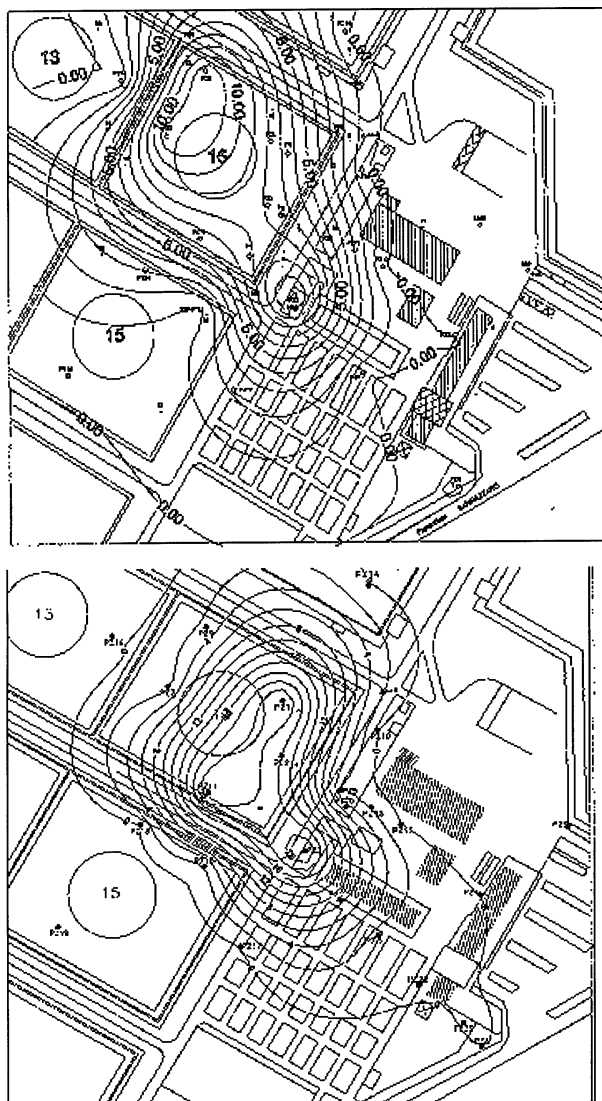
Figure 3:   The concentrations dissolved hydrocarbons in A) September 1996 and B) March 1998. The contour spacing is at 1 mg/l
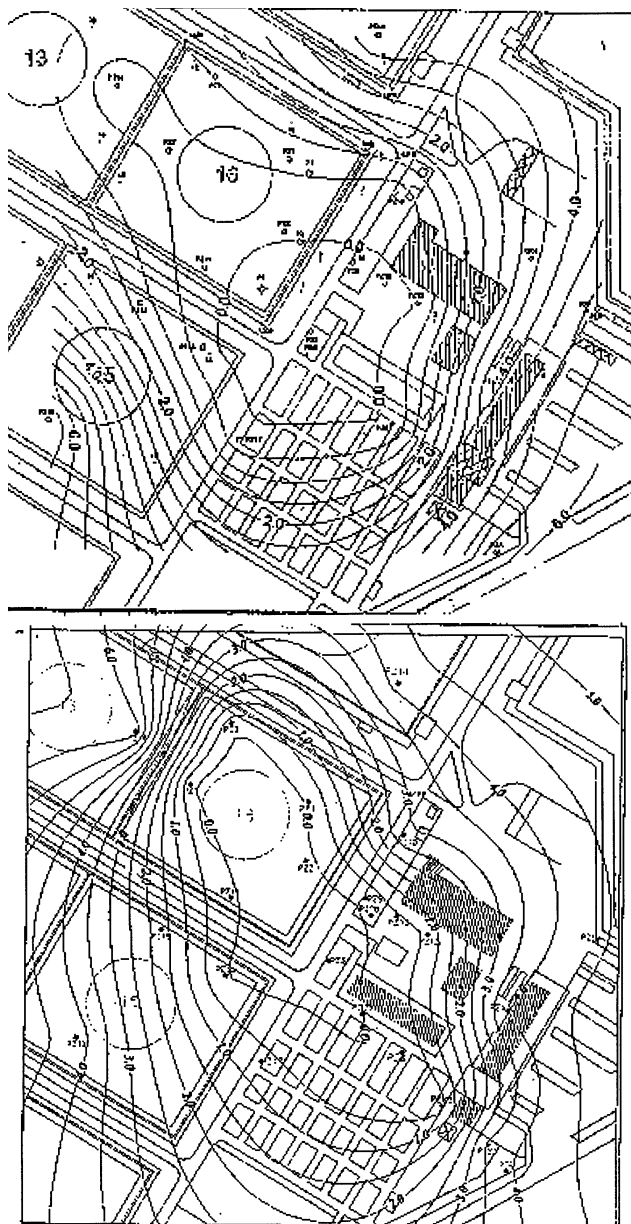
Figure 4:   The oxygen concentrations in mg/l at A) September 1997 and B) March 1998.

Conclusions

At an industrial site contaminated with petroleum hydrocarbons, different analytical campaigns were performed in order to verify the presence of intrinsic bioremediation.

Analytical and microbiological data-supported the hypothesis that intrisic bioremediation is occurring and confirmed that a well defined aerobic and anaerobic biodegradation is active throughout the site.

Monitored Natural Attenuation – Considerations of its Application on Contaminated Sites in Poland (Piotr Cofalka, Institute for Ecology of Industrial, Poland)

Abstract

It is very difficult to define criteria that should be used for choosing a method for a site remediation. All decision-makers have to take into account social and economical aspects. But there are also scientific criteria that should support their decisions. They define the method of remediation regarding human safety and the environmental impact. This work is proposing criteria for application of remediation method (among them Monitored Natural Attenuation) in Poland. They are not yet applied by governmental institutions because the appropriate legislation will be created in the future. Proposals described here could be taken into account when creating a new law related to environmental issues.

1.   Introduction

The problem of controlling contaminated sites is very common in most industrialized countries and in areas used by the army. Often, site remediation costs are very high because of expensive technologies used for that purpose. In some cases monitored natural attenuation (MNA) that allows reduction of the total clean-up costs can be used. However there are some criteria that have to be taken into account before the method is used. From the scientific point of view during the remediation process two main goals should be achieved: to clean up the site successfully and to avoid any harm to people and their environment . For this purpose, necessary tools being developed by scientific societies to create a support system for decision-makers.

2.   Criteria for Mna Application

The issue of monitored natural attenuation refers mostly to contaminated soil and ground- water. Pollutants are usually located in the soil and transported by the carrier fluid, water. This way some amount of contaminants appears in the pathway(s).

Before it is decided which method of remediation can be used, it is necessary to pass through the following steps:

• identify all pollutants present at a site,

• assess the risk for environment and humans considering each of the pollutants,

• investigate the groundwater velocity and dispersion,

• assess an amount of pollutant(s) located in the site,

• analyze available physical, chemical and biochemical methods of degradation or attenuation of the pollutant(s),

• calculate the duration of remediation process for all different methods of remediation,

• assess the cost-effectiveness for all available methods,

• investigate the social reaction proposed methods,

• choose and apply the appropriate method for remediation.

All these steps create an algorithm based on scientific and socioeconomic criteria. Now we will try to discuss some of scientific ones.

2.1.   Identification of Contaminant(s)

Pollutants residing at the site must be correctly identified to investigate methods of degradation or attenuation (if any exist) and assess the risk for humans and the environment. This criterion determines a possibility of MNA application very strictly. MNA must not be used in the conditions of unidentified contaminants.

To be able to identify the chemical compound residing in the soil or in the groundwater, it is necessary to take several samples. But it is important to do it appropriately. There is a risk that soil sampling will speed up dispersion of the

contaminant or damage the natural barrier separating contaminant from the groundwater (i.e. a clay layer). That's why the sampling procedure requires a special care and analysis of the geological structure of the site.

2.2.   Risk Assessment

A very important factor that should be taken into account is a risk assessment. It must be done carefully and the risk for humans, animals, plants and other elements of the environment must be analyzed. All possible transport media must be identified. The contaminant may reside in the soil, but there can exist a possibility of transformation, i.e. a liquid or solid substance may change into gas. In those cases, conditions of contaminant dispersion may change completely. Then they are dependent on the wind (direction, velocity), temperature, humidity, etc.

The risk assessment requires analyzing of many scenarios. In each of the cases we need to know if there is a possible negative influence on humans or their environment. If so, we have to predict the scale of this negative impact and its probability. Only completely safe methods may be applied; that's why it is necessary to investigate so many different cases. If one of the cases is omitted then a danger arises that our method is not only unsuccessful but also harmful.

2.3.   Dispersion of Contaminant

Geological structure of the contaminated site is essential for contaminant dispersion. In some conditions chemical compounds can propagate very fast, and another time the whole amount of contaminant resides in almost the same place all the time.

Different types of contaminants can have different transport mechanisms. They can be present as solids, easily soluble or insoluble in water, light non-aqueous phase liquids, or dense non-aqueous phase liquids. In most cases, the medium that distributes the contaminant is groundwater. To obtain any information on the intensity of the dispersion process we have to know the hydrogeological structure of the site.With this knowledge it is easy to predict how far contaminants can be distributed after a period of time or how quickly they will reach receptors.

The application of MNA is based on a detailed site characterization. This part of investigation may be expensive, but there is no appropriate model without data. That's why we have to know as much as possible about the site.

The plume must be monitored in order to assess if there is an expected attenuation. We have to control it, because uncontrolled dispersion of the contaminant may cause it to reach receptors that should be protected. In such a case MNA wouldn't be a successful method.

2.4.   Amount of Contaminant Located In-situ

The concentration of the contaminant often determines the method we can choose for remediation. Sometimes the area of the site and the amount of contaminant are so huge that active remediation methods are not cost-effective. MNA is generally a method that reduces the concentration of contaminant slowly. During the remediation process we have to control if the contaminant concentration is decreasing and whether there is any progress in this process. It may happen that, during the MNA process, the concentration of contaminant increases and we cannot identify the reason. Is such a case there should be applied an alternative remediation method. Distribution of contaminant impacts the area where the contaminant resides. Usually water distributes the contaminant in various directions, creating a plume. Depending on the intensity of the transport of contaminantk, its concentration can decrease relatively slowly or fast. That is why it is necessary to investigate if intensity of dispersion corresponds to intensity of bioremediation processes. This way the plume will not extend and will not reach potential receptors and therefore there is no risk for them. Beside the biodegradation, there are other processes that lower the contaminant concentration (e.g. sorption, dilution), but it is essential to investigate their impact for potential receptors.

2.5.   Methods of Degradation or Attenuation

According to the US EPA definition of natural attenuation, the main goal of passive remediation is to attenuate or degrade the contaminant placed in soil or groundwater. This aim can be achieved by dilution, dispersion, (bio)degradation, irreversible or reversible sorption and radioactive decay of contaminants. All these methods lead to a net reduction of contaminant toxicity and risk for humans and their environment. Observing the natural attenuation at the characterized site the mechanism of this process can be explained. There is a possibility to create a model of the natural attenuation for a category of similar cases (similar substances and sites). Such a model enablesusers to predict duration and efficacy of the natural attenuation for other sites of this type. However, the success of remediation depends mostly on accurate site characterization.

2.6.   Duration of Remediation Processes

Natural attenuation as a remediation strategy has to be calculated in time frames as precisely as possible because it is connected with risk assessment. Decision-makers must be sure that a proposed method is safe for humans and their environment.

In some cases it is not so important how long it takes to clean up the contaminated area. But more and more often, the considered area is taken into account as land for new buildings, parks or other kinds of investment. These circumstances often limit the time period dedicated for the remediation. In practice it means that MNA is not accepted as a strategy of remedy in these cases.

2.7.   End-products and By-products

Natural attenuation often leads to transformation of toxic substances into other compounds. The daughter products are usually safe for humans and the environment. But it does not happen always. Sometimes they still are not environment-friendly. However, if the parent products were more harmful for the environment than final products, this type of natural attenuation is successful. Another problem appearing at sites is the impact of by-products. They can be more harmful compared to parent products, and therefore, it is so important to assess the risk posed by parent products, by-products and final products of processes occurring at the site.

A large number of conversions of chemical compounds, especially inthe case of organic compounds, increases the probability that some compounds may negatively impact the environment. They may lead to a temporary increase of substances that are more toxic than the original compounds that reside at the site. If only this phenomenon leads to the final degradation of the parent substance, it is suggested to consider the risk for receptors and to decide if natural attenuation is a desired method.

In some cases, a chemical compound may be converted to a new substance, without enough information about the risk that this new substance brings to human health and the environment. Such cases should be eliminated in monitored natural attenuation.

2.8.   Mna Tools Necessary for Decision-makers

In cases where the transport of a contaminant is extensive, it is necessary to decide if natural attenuation is a satisfactory strategy or if it should be replaced by other active methods to avoid a risk for humans and the environment. To be able to conduct such an examination, decision-makers require appropriate tools. Universities and research institutes attempt to implement such tools investigating different sites, different contaminants, changing geological and hydrological conditions, analyzing microorganisms and bacteria that speed up degradation of toxic substances, and comparing different physical and chemical factors that have an influence on the natural attenuation. On the basis of this knowledge, models are used as guidelines for natural attenuation application. Having a good model and a properly characterized site it is simple to predict a time frame for the site's clean-up. If the predicted period of time is not acceptable, it means that natural attenuation should be supported by other methods. However, it should be remembered that natural attenuation combined with another method must not be disturbed.

3.   Decision-making on MNA Application

To make decisions about MNA application the following procedure must be performed (the algorithm is shown in Figure 1).

The procedure usually starts from a review of site-specific and historical data that will allow creating a conceptual model. In this step pathways, located receptors, and comprehended hydrological data must be identified. A conceptual model assessing natural attenuation is created in the next step. To develop the model it is usually necessary to perform additional site characterization. The main aim of this stage is to decrease the uncertainty and to obtain enough data for simulation. The data gathered during additional site characterization leads to the revision of the model. Some hypotheses are confirmed and other are negated. The new model allows starting a simulation process, which gives answers about time frames and risks for human health and/or environment. This step of the algorithm should predict the rate at which natural attenuation proceeds (it depends on the type of processes that are performed at the site). The score of the simulation decides if the MNA method is suitable for the investigated site or not. Depending on the method of attenuation, a relevant long-term monitoring and a contingency plan must be considered. These provide control of the occurring processes and allow change to the remedy strategy if MNA is not successful.

Nowadays in Poland there are no tools available for investigating MNA strategies for decision-makers. The only way to assess the efficiency of this method is a co-operation with scientific institutions (universities or research institutes). However, not many scientific institutions and local communities know MNA as a strategy for site remediation. It can be expected that this method will get more popular in a few years in Poland, as it is more cost-effective than active methods of remediation.

4.   Background of Natural Attenuation in Poland

4.1.   Most Common Types of Contamination in Poland

In Poland most contaminated sites contain hydrocarbons (polyaromatic and alifatic), heavy metals or toxic inorganic compounds. There are many sites which are brown-fields or landfill from the heavy industry in the Silesia region. Most
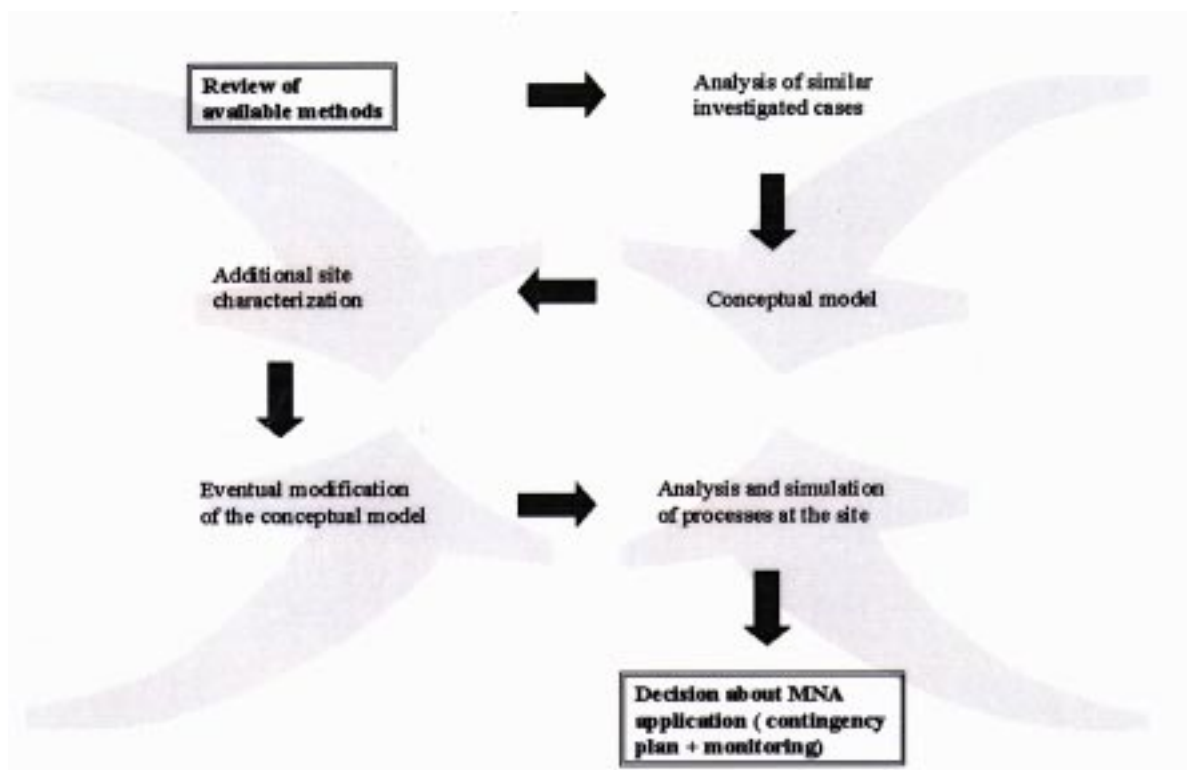
Figure 1. The algorithm for making decisions on MNA application.

common contaminants found there are lead, cadmium, zinc, boron, barium, mercury and heavy hydrocarbons. Other investigated places are the former Soviet Union military bases and military bases of the Polish Army. In many cases there were found underground tanks with fuel that are sources of plumes. Large amounts of fuel were also found in groundwater near the fuel stations. Next to jet fuel, there are also appearing chlorinated solvents appear used for cleaning military equipment (tanks, airplanes).

Poland does not use atomic energy in its economy. Therefore the problems with storing of radioactive materials are eliminated. The only experimental atomic reactor in Œwierk storesits radioactive wastes in controlled conditions.

4.2.   MNA as a Remedy Strategy

Natural attenuation is not officially used in Poland as a remedy strategy and this method is not common in our country yet. But there are more and more cases of natural attenuation application in foreign countries like the USA, Germany, and the Netherlands.

It must also be mentioned that there are many contaminated sites in Poland where active remediation was not applied due to lack of funds. These places are monitored and sometimes processes are observed leading to natural attenuation. Decision-makers decide to wait for funding and in their opinion the active remediation action at the site is not a priority, because the risk for receptors is often insignificant and the amount of contaminant is still decreasing. This way they accept natural attenuation strategy involuntarily. The strategy does not contain a contingency plan, but this is already a simple form of this type of remediation. It can be expected that natural attenuation will be developed in Poland in future and finally appropriate legislation and tools for application of MNA like those existing in the USA (e.g. EPA directives, MNA toolbox), Germany and the Netherlands, will be created.

4.3.   Polish Law and MNA

The prime regulation regarding environmental protection is The Law on Protection and Conservation of the Environment (1980). The Minister of Environmental Protection supplements the Environmental Law with Ordinances (concerning air pollution control, wastewater control, wastes, noise, and financial regulations affecting use of the environment).

In 1974 the Water Law was issued containing regulations of water resources and their protection. In 1995 a new version of the Law on Area Development created concerning aspects of land-use. Up to the present, only one official list of contaminant concentrations in soil was compiled. It is contained in the Ordinance of 1986 issued by the Minister of Environment on agriculture use of sediments from water treatment plants and concerns only chosen heavy metals. There have been, however, some guidelines published specifying acceptable contaminant concentrations. The most common is the document issued in 1994: "Methodology Guidelines for Assessment of the Level of Contamination in Soil and Groundwater with Petroleum Products and Other Chemical Substances for Remediation Purposes".

Unfortunately there are no sufficient guidelines concerning application of different methods of remediation. Therefore some research institutes and universities make an effort to prepare a proposal of regulations and guidelines which concern different remedy strategies. Monitored natural attenuation should be placed in these proposals as a cost-effective method that can be applied in suitable conditions.

References

Assessment of Harms Made by the Army of Russian Federation. Borne Sulinowo - Final Report. State Inspectorate For Environmental Protection and Military Technical Academy. Warsaw 1993.

Recognition of Soil and Groundwater Contamination with Chemical Substances, Military Toxic Substances and Radionuclides - Borne Sulinowo. Military Technical Academy, Warsaw 1993.

International Experience and Expertise in Registration, Investigation, Assessment, and Clean-Up of Contaminated Military Sites. Umweltbundesamt, Berlin 1997.

Applications of Monitored Natural Attenuation in the United States (Fran V. Kremer, United States Environmental Protection Agency)

Abstract

There has been increased interest in the United States in the application of monitored natural attenuation (MNA) for remediation of hazardous wastes. A policy for its use for ground water and soil has been developed. Data are available on national trends for the use of MNA for abandoned hazardous waste sites and for underground fuel storage tank sites.

MNA Directive for Ground Water and Soil

MNA is defined as the use of naturally occurring attenuation processes within the context of a carefully controlled and monitored site cleanup approach that will reduce contaminant concentrations to levels that are protective of human health and the environment within a reasonable time frame (1). MNA processes include physical, chemical or biological processes that act without human intervention to reduce the mass, toxicity, mobility volume or concentration of contaminants. This includes destruction of contaminants, biodegradation, chemical or biological stabilization, dispersion, sorption, volatilization or dilution. EPA prefers those processes that degrade contaminants and expects that MNA will be most appropriate where plumes are stable.

Some processes can have undesirable results such as creation of toxic daughter products or transfer of contaminants to other media, presenting an additional problem.

Some have perceived the use of MNA as a "walk away" or "do nothing" approach. In selecting any remedy for site remediation, the goal is to protect human health and the environment. In using MNA, the goals remain the same. The use of MNA involves site-specific, risk-based decisions. The proponent must demonstrate that MNA is an appropriate option.

To demonstrate that MNA is an effective option, three types of site-specific information may be required:

1. Historical ground water and/or soil chemistry data to demonstrate a trend of declining contaminants concentration.

2. Hydrogeological and geochemical data to demonstrate MNA processes and rates.

3. Field or microcosm studies.

Unless item 1 is of sufficient quality and duration, number 2 is generally required. This is a regulatory decision.

MNA will typically be used in conjunction with active remediation measures (e.g. source control) or a follow-up to such measures. MNA should not be used where such an approach would result in significant contaminants migration or unacceptable impacts to receptors.

The time frame for MNA to meet remedial cleanup goals should not be excessive compared to that required for other remedies. The development of this reasonable time frame is a site specific decision. Some factors that impact the "reasonableness" of the time frame include:

1. Current and potential future uses of the affected media

2. Relative time frame in which the ground water or property may be needed.

3 Public acceptance of the time frame for remediation

4. Reliability of monitoring and institutional controls, adequate finding over the time required to reach cleanup objectives

5. Regional resource issues such as impacts on the larger airshed or watershed.

One of the critical aspects in using MNA is source control measures. EPA expects that source control measures will be evaluated for all sites and implemented at most sites where practicable. Measures include removal, treatment or containment of sources.

Another critical component of MNA is performance monitoring. This is required to ensure that the attenuation processes are proceeding as expected and to ensure protectiveness of human health and the environment. This is especially important as MNA generally involve a longer clean up times, as in many in situ treatment processes. Monitoring is required as long as levels remain above cleanup goals.

Contingency remedies are an important component for MNA. A contingency remedy is a cleanup technology, process or technique that will function as a "backup" in the event that MNA fails to perform as expected. Contingency measures are particularly important when MNA is based primarily on predictive analysis. Triggers should be established that identify unacceptable performance of the MNA remedy and the need for a contingency remedy.

The Directive can be obtained electronically at the following web site: *http://www.epa.gov/swerust1/directiv/9200417.htm.*

Trends in the Use of MNA

MNA is being used under several regulatory areas in the United States. This includes the fuel underground storage tanks, and abandoned and active hazardous waste facilities. MNA is also being used under state voluntary cleanup programs and for Brownfield sites. Data nationally have been compiled on the abandoned hazardous wastes sites (Superfund sites) and for the underground storage tank sites.

For the Superfund sites, Figure 1 shows the actual numbers and percent of all Superfund sites where MNA was selected for ground water Records of Decisions (RODs). As the data indicate, in 1997, one-third of the RODs incorporated MNA in some manner in a site remediation. Figure 2 depicts the types of contaminants where MNA was selected for ground water, with solvents and metals contaminants comprising the majority of the sites. Figure 3 shows the types of sites where MNA was selected for ground water contamination with nearly half of these sites being landfills.

For the leaking underground storage tank (LUST) sites, data collected by the Office of Underground Storage Tanks show that MNA was chosen for almost half of the sites (Figure 4). With the introduction of methyl tertiary butyl ether as an additive in gasoline in the U.S., this distribution may change. For LUST soil applications, MNA was used at less than 10 percent of the sites in 1997 (Figure 5).

Summary

MNA can be utilized at many sites. Use of MNA does not imply a "walk away" or " do nothing" approach. MNA involves an active choice and justification for use in employing a passive remediation approach. It requires careful monitoring and use of contingency measures in the event it does not proceed as expected. The cleanup is not complete until the cleanup objectives, set by the regulatory agency, have been met. More data and technical guidelines (2) are being accrued to define the appropriate applications for the use of MNA. Given this experience, we will have a better understanding of its appropriate uses and limitations in protecting human health and the environment.
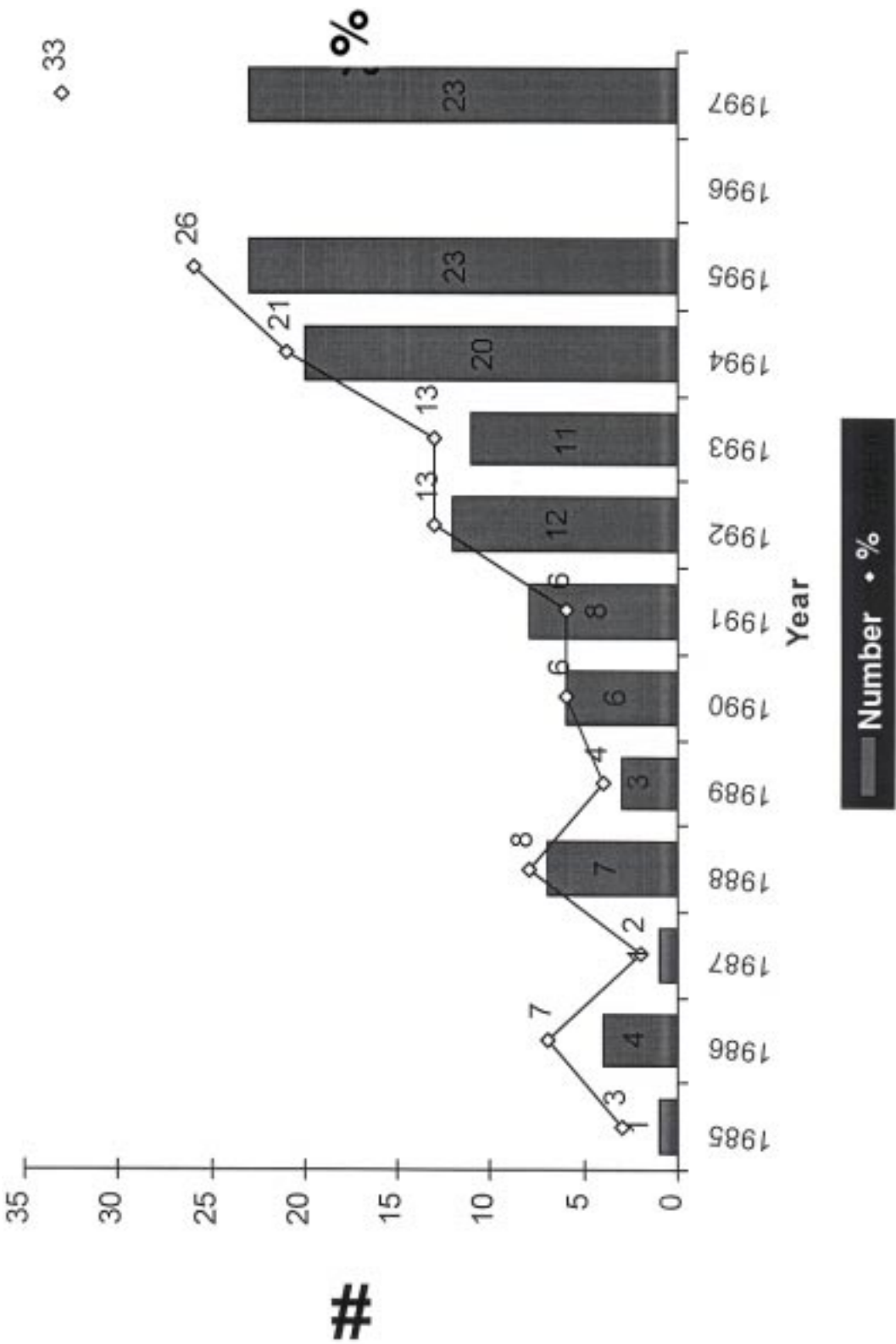
Figure 1.   MNA groundwater RODS.
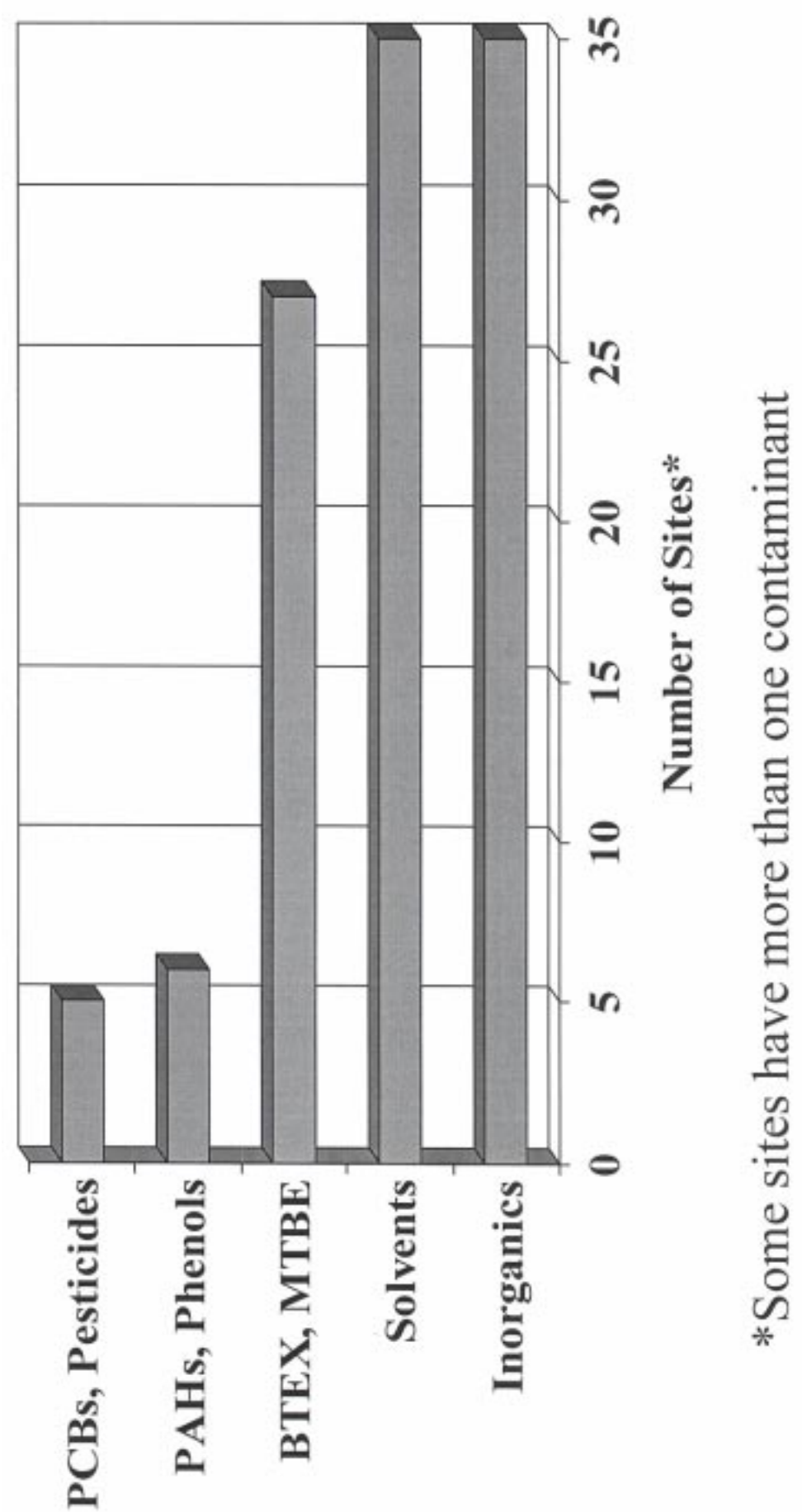
Figure 2. Contaminants present at sites for which natural attenuation was specified.
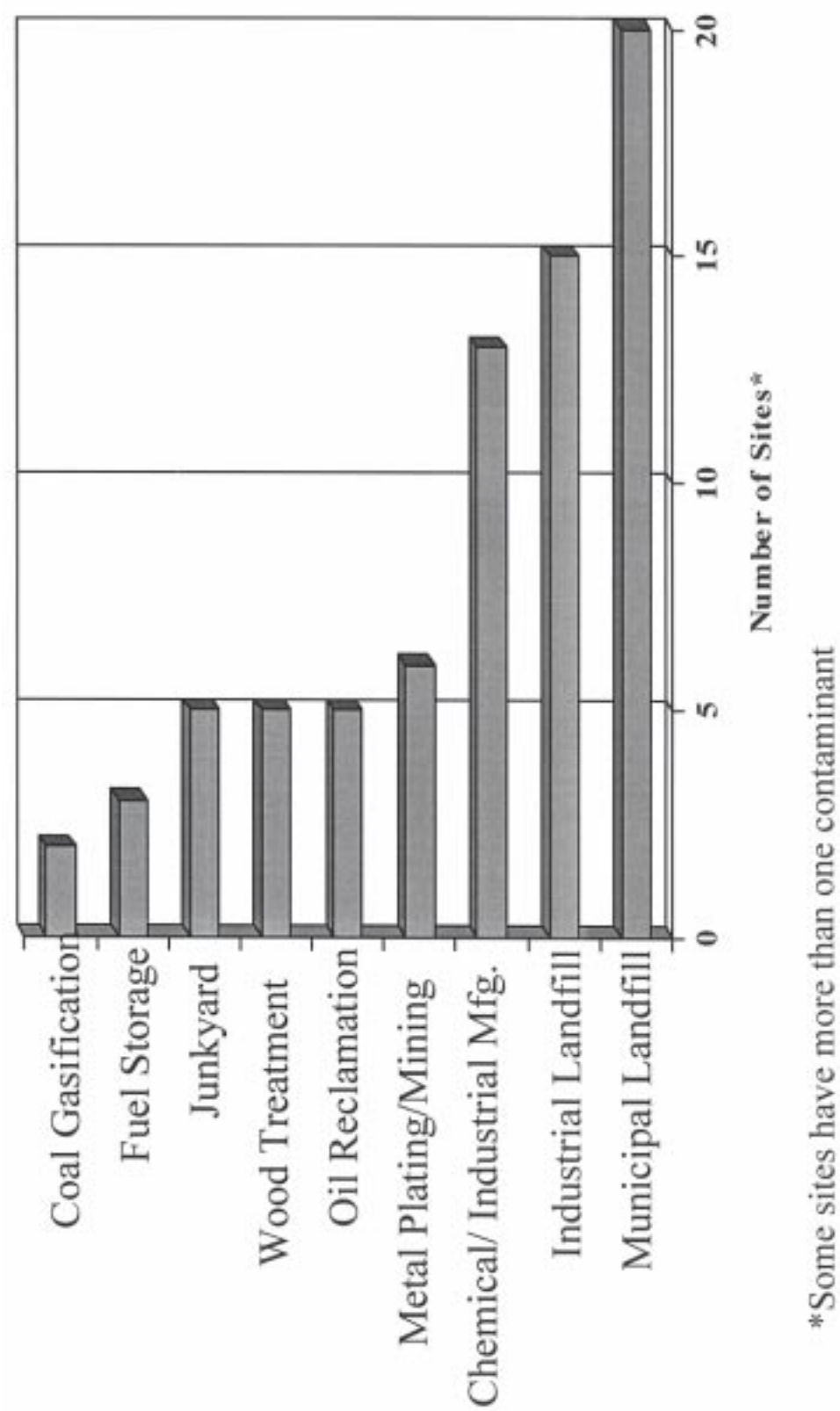
Figure 3.   Contaminants present at sites for which natural attenuation was specified.
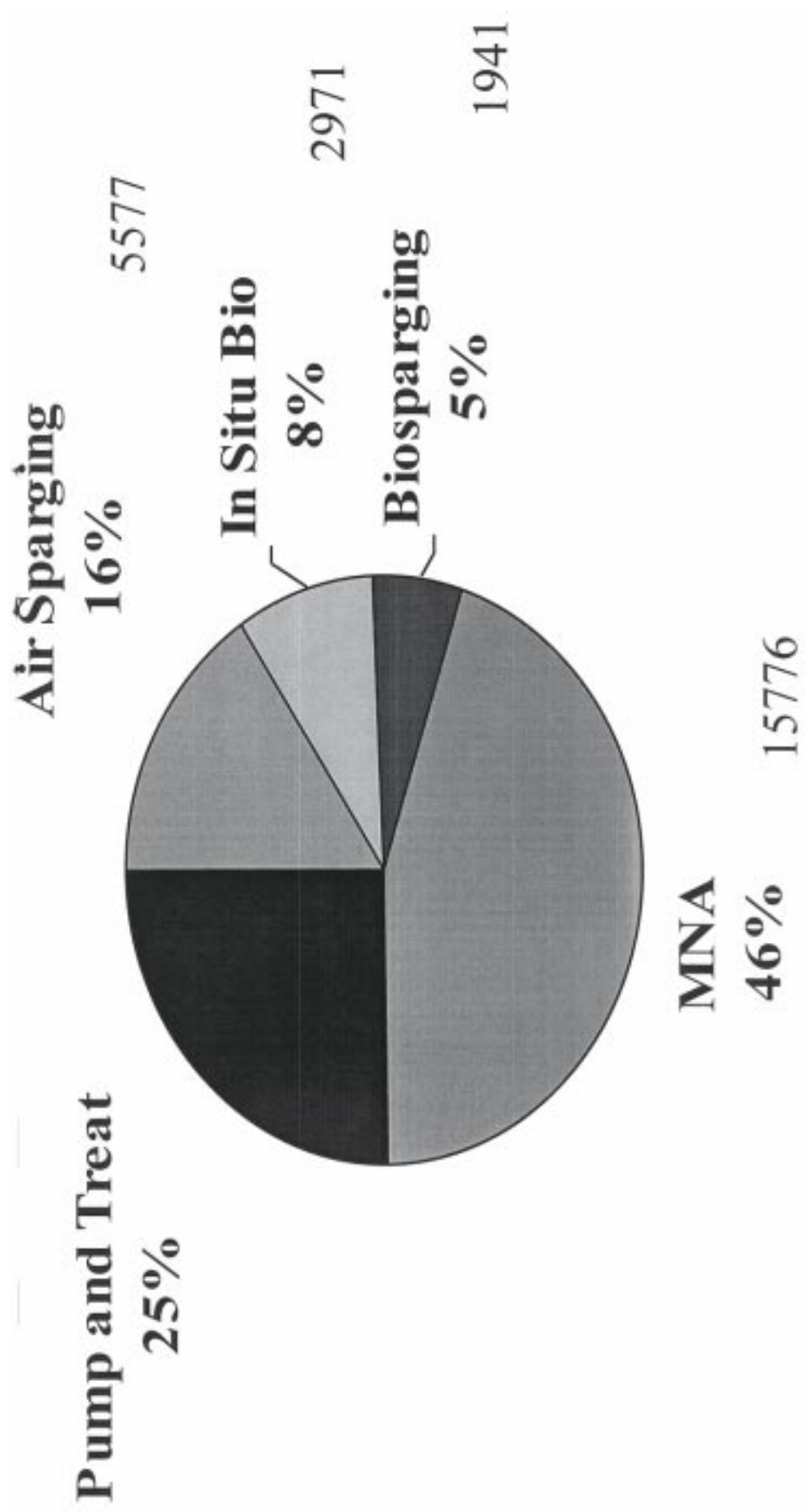
Figure 4. LUST groundwater remediation technologies, FY97.
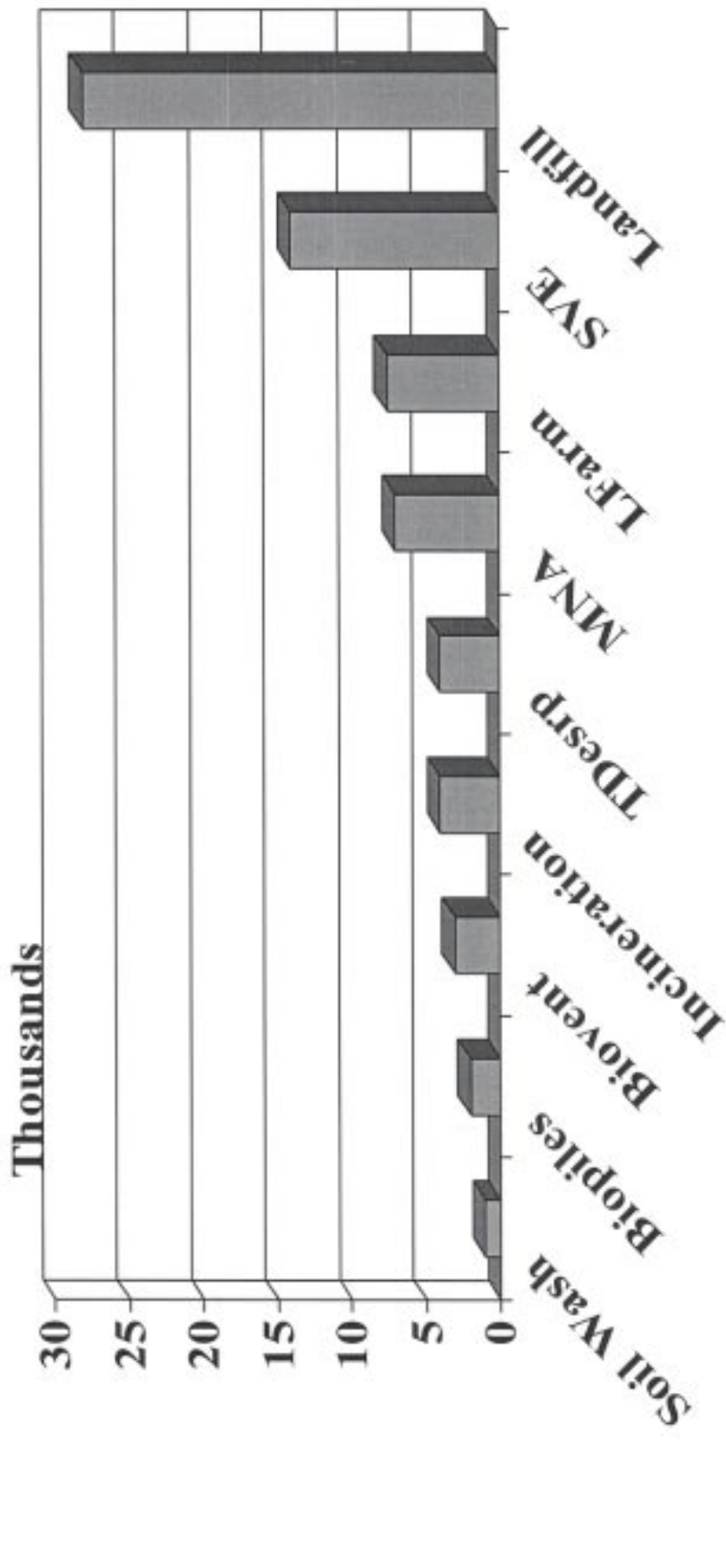
Figure 5.   Soil remediation technologies at UST sites, FY97.

References

"Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites", U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Directive 9200.4-17, April 21, 1999, Washington, D.C.

"Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water" U.S. Environmental Protection Agency, Office of Research and Development, EPA/600/R-98/128, September 1998.

Promoting the Acceptance of Monitored Natural Attenuation (Anja J.C. Sinke[1], Timo Heimovaara[2], Haimo Tonnaer[3], and Johan van Veen[1] [1]TNO, Apeldoorn, NL, [2]IWACO, Rotterdam, NL [3]TAUW, Deventer, NL)

Introduction

Monitored natural attenuation (MNA) at contaminated sites is a rather new phenomenon in Europe. The acceptance of MNA as remedial strategy strongly depends on the regulatory framework, the understanding of the processes in the soil and the actual experience at contaminated sites. To enhance the acceptance of MNA as remedial strategy all actors, such as the regulatory agencies, site owners, consultants and the public, have to be convinced that it is a reliable approach.

To promote the application of MNA as a cost-effective and risk-based approach at contaminated sites several actions have been taken:

I.   development of a decision support system including the formulation of a measuring strategy

II.   demonstration projects where MNA is being implemented

III. development and organisation of MNA courses

IV. publications in (common) journals, and presentations at workshops

I.   In the Netherlands a decision support system (DSS) has been developed in a NOBIS project which provides a stepwise approach to judge the potential for MNA as remedial strategy at a specific site (Sinke et al. 1998) The DSS is formulated for the two most common mobile pollutants: chlorinated solvents and BTEX. It includes a quick scan that gives information on the chance that MNA is a reasonable alternative at a given site. It has been tested at several field locations in a NOBIS project supported by 15 parties from industry and authorities. The system is a communication tool in the discussions between landowners and regulators on the decision of how to approach a contaminated site. The DSS will be discussed in detail below.

II.   Demonstration projects help to convince people that in specific cases MNA is a reliable strategy. Clearly MNA as remedial solution is location-specific and has to be intensely controlled. In the Netherlands MNA is seen by the authorities as an "experiment" under controlled conditions (Vegter, this issue). So to apply MNA at field locations the authorities provided some room for these experiments in terms of time and space. At the moment MNA is studied at approximately 25 sites throughout the Netherlands.

III. As MNA is a relatively new "technique," the local consultants and authorities have little experience and know-how of the underlying processes and the quantification of these processes. Workshops and courses have been organized to transfer the knowledge on MNA to a broader public. Some of these courses have been focused very specifically on the geochemistry, the biology and the hydrogeology of MNA; other courses have been focused more on the regulatory constraints.

IV. The publications in journals, and presentations at workshops contribute to the acceptance of MNA as people become more acquainted with the possibilities and the restrictions of MNA.

Nobis Decision Support System

In the Netherlands a decision support system (DSS) has been developed in a NOBIS project which provides a stepwise approach to judge the potential for MNA as remedial strategy at a specific site. The DSS is formulated for the two most common mobile pollutants: chlorinated solvents and BTEX.

The system includes listings of the scientific arguments which have to be thoroughly evaluated for each specific site. Also political and practical aspects such as urban planning, changed (future) use of the site, time frame involved and liability should be considered.

The DSS is depicted as a "natural attenuation route" with four "traffic lights" (Figure 1, Table 1). In each phase at the sequential traffic lights, the chances of natural attenuation as a remediation option are determined as good (green light),
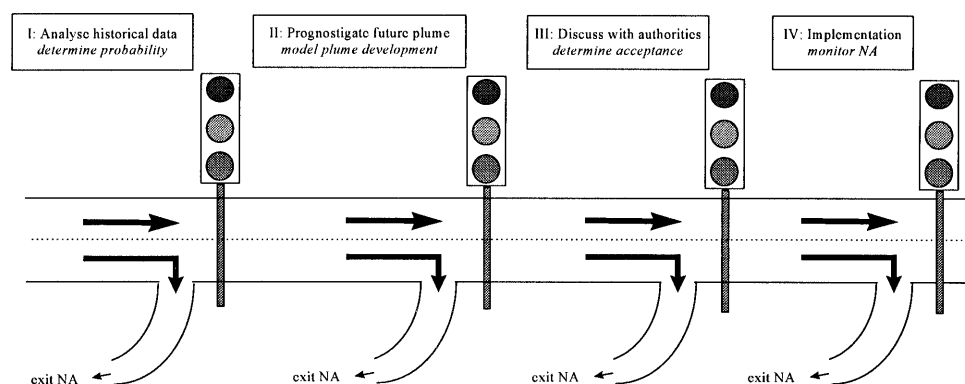
Figure 1.   The Dutch Natural Attenuation route with traffic lights

Table 1.   Description of Activities to be Carried Out for Each Traffic Light.

Traffic light	Activity	Additional remarks
1	analyze data and determine chance on biodegradation	index
	collect additional data in field or laboratory	depends on results in **(1)**
2	use a solute transport and fate model to calculate:	
	• the decrease in amount of contaminant with time	
	• the change in position of the center of the pollutant	
3	discussion between authorities and problem owner	
4	prepare a long-term monitoring plan	
	• to evaluate the used model and efficacy of MNA	
	• to protect surrounding objects	

fair chance (orange) or no chance (red). In case the traffic light remains orange, additional information has to be collected.

The first two traffic lights are based on technical and scientific information and can be used to evaluate existing data on whether natural attenuation is occurring, to identify and collect additional data and to prognosticate the long-term behavior of the plume. Based on the results collected at the first and second traffic lights, at the third traffic light the decision on whether NA will be applied at the given location is taken. The decision depends on the discussion between problem owner and authorities. Besides scientific arguments, political and practical aspects may play a role in the final decision and those aspects are listed in the report to be consulted at each traffic light.

At the fourth traffic light NA is implemented. The model gives suggestions for a monitoring strategy that is focused on verification of the assumptions of future behavior and on protection of local receptors. Finally the monitoring of the location may be stopped.

As the model is based on the current technical and scientific state of the art, it is expected that it will be subject to continuous adaptations. A draft version (version 1.0) of the decision support model has been tested at several Dutch locations.

Measuring Strategy

A good measuring strategy is the basis for reliable decisions on the application of MNA. Generally in the Netherlands, the characterisation of a contaminated site has been focussed on quantifying the extent and amounts of the pollution, which implies that especially near and around the source zone where the highest concentrations are found, numerous measurements are done. However, to quantify the rate and efficacy of natural attenuation, the position of the sampling wells has to be focussed on describing the concentrations and trends in the plume. This implies that the position of the sampling wells has to be in parallel with the groundwater flow direction (Figure 2). To establish the lateral spreading of the plume one or two transects perpendicular to the groundwater flow direction have to be measured as well. Also the pristine acquifer upstream and down stream of the plume has to be characterized in order to have a background reference.

First Traffic Light: Analyze Data and Determine the Chance on Biodegradation

Goal is to make as early as possible with as little expenses as possible, a good estimation of the probability that monitored natural attenuation is an appropriate strategy to achieve site specific remediation objectives within a reasonable time frame. This first traffic light is actually a quick scan of the historical data that gives information on the chance that MNA is a reasonable alternative at a given site. As chlorinated solvents and BTEX compounds behave quite differently and have different degradation characteristics, the information used and the resulting indices are different for these compounds. In the draft version the quick scan for chlorinated solvents has been formulated while the quick scan for BTEX is still under development.

Chlorinated Solvents

To carry out the quick scan for chlorinated solvents only a restricted number of parameters has to be measured: concentration of parent compounds, concentration of daughter products and eventually the redox characteristics and concentrations of dissolved organic carbon. To make a first rough estimation on the occurrence of natural attenuation, the chlorine index has to be calculated in a series of wells that are positioned parallel to the groundwater flow (Figure 2). The chlorine index indicates the averaged number of chlorine atoms on the solvent (PCE=4, TCE=3, DCE=2, VC=1, ethene=0). The idea behind the chlorine index is that the major degradation pathway is anaerobic dechlorination. This is especially true in the Netherlands where, generally speaking, anaerobic conditions prevail in the groundwater. The combination of the alteration of the plume, the chlorine index and the trends in the chlorine index determine whether MNA is a remedial option at the site or not (Table 2).

Formula of the chlorine index:

$$chlorine \cdot index = \frac{\Sigma N_d * metabolites}{\Sigma total solvents}$$

First Traffic Light (Extended): Collect Additional Data in Field

When the first traffic light is "orange" additional information has to be collected on the potential of the site to degrade the contaminants. The redox conditions at the location have to be characterized according to Figure 3. The characterization is simple as only three categories are distinguished: aerobic, anaerobic and strongly anaerobic.

The redox has to be characterized for each individual sampling point and compared to the "potency" table (Table 3). In this table the possibilities of degradation of a single compound under the given redox is given as likely (score 1), not known or indifferent (score 0) or unlikely (score -1). For each sampling point the redox is characterized and the redox score summed. For instance, the presence of PCE and TCE under aerobic conditions gives a score of -2 (-1 and -1). When also VC is present in the same sampling well (+1), the total score for the well is -1. The average redox score at the location and the trends in the score determine whether NA of chlorinated solvents is a remedial option at the site or not (Table 4).
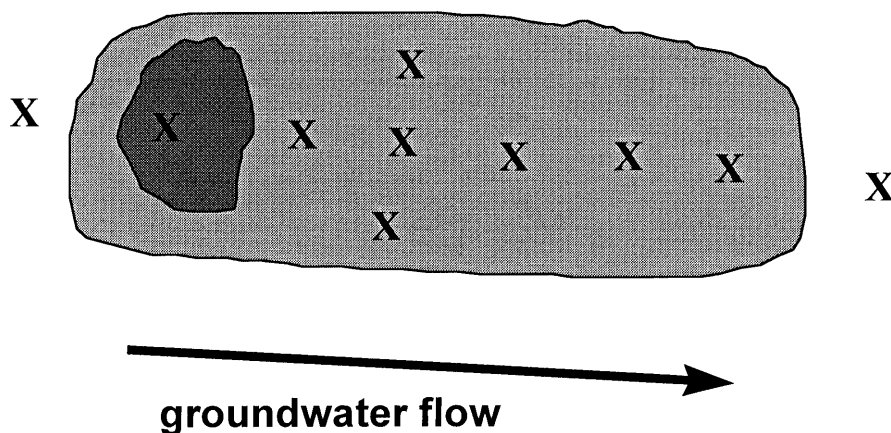

Figure 2.   Schematic representation of the optimal position of the sampling wells.

Table 2.   Scheme to determine whether NA has a chance to be appropriate at a PCE contaminated location based on the alteration of the pollution, the chlorine index and the trends in chlorine index.

Age of plume	chlorine- index	trends in chlorine-index	chance of NA
age > 3 years	$\gg 3$	irrelevant	red: poor chance
age > 3 years	2 - 3	index stable with time or with distance to source	red: poor chance
age > 3 years	2 - 3	index decreasing with time or with distance to source	**orange: fair chance,** collect additional data
age > 3 years	$\ll 2$	irrelevant	green: good chance
age < 3 years	no metabolites		red: poor chance
age < 3 years	metabolites present		green: good chance
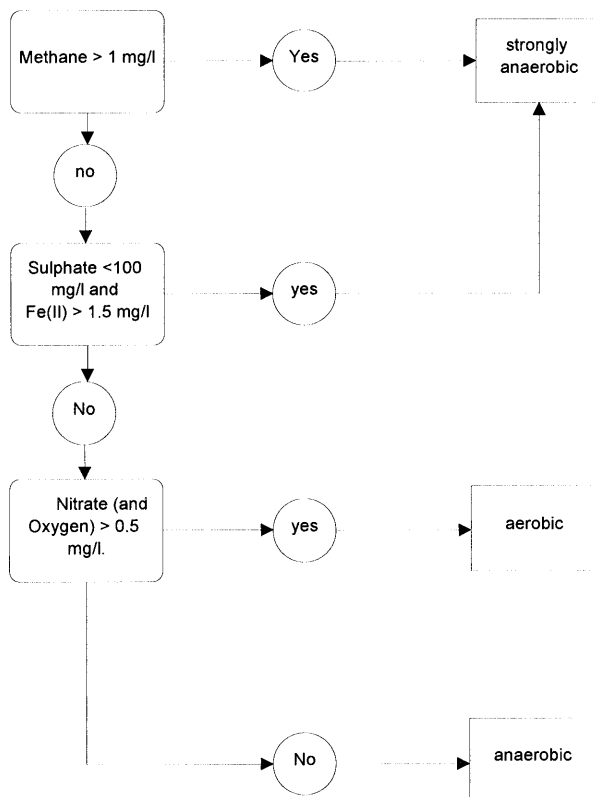
Figure 3.   Flowchart to characterize the redox conditions.

Table 3.   Potency Table to Determine Whether the Redox Score ts Positive (1) or Negative (-1)

Redox conditions*	PCE	TCE	CIS	VC
oxic (aerobic)	-1	-1	0	1
anaerobic	-1	-1	0	0
strongly anaerobic, DOC** < 5 mg/l	-1	-1	-1	-1
strongly anaerobic, 5 < DOC** < 10 mg/l	0	0	0	0
strongly anaerobic, DOC** > 10 mg/l	1	1	1	1

* For each sampling well the redox is characterized according to Figure 2 and the redox score is determined at a value between -4 and +4.
**DOC: the total amount of dissolved organic carbon which in some cases also includes co- pollutants such as BTEX or phenols.

Table 4.   Chance of Using NA Based on the Average Redox Score and the Spatial and Temporal Trends

Average redox score in existing monitoring wells	trends in score spatial or temporal	chance of using MNA
redox score $\ll$ 0	decrease with time or distance	red: no chance
redox score $\ll$ 0	increase with time or distance	orange: fair chance
0 $\ll$ redox score $\ll$ 1	decrease with time and distance	orange: fair chance *
0 $\ll$ redox score $\ll$ 1	increase with time or distance	green: good chance
redox score > 1	trends irrelevant	green: good chance

* A fair chance with a decreasing redox score with time or with distance has to be seen as a warning that the degradation might not be complete but stagnate at some metabolite.

Second Traffic Light: Use a Solute Transport and Fate Model

At the second traffic light a solute transport and fate is used to model the expected behavior of the plume. Several models may be applied: MODFLOW with RT3D, METROPOL, BIOSCREEN, VERA. The models have to be based on field parameters (Table 5) and have to calculate:

- the decrease in amount of contaminant with time

- the change in position of the center of the pollutant

The results of the modeling exercise are to be given in two figures depicting the load in the plume and the development in polluted area (Figure 4). Based on these two figures, it is possible to say on a technical scientific basis whether MNA is a viable remedial option or not.

2   increase in load and increase in polluted area: *no chance*

3   increase in load and stable area (unlikely scenario): *fair chance, depends on availability of space and time*

4   decrease in load and increase in polluted area: *good chance, depends on conditions such as available space and time*

5   decrease in load and decrease in polluted area: *good chance, depends on time scale.*

Third Traffic Light: Discussion Between Authorities and Problem Owner

At the third traffic light it is clear that on technical scientific criteria MNA is a valid remedial option. However, the decision on the actual implementation depends on a range of other criteria and is discussed between problem owner and (local) authorities. The DSS gives no guidelines for the evaluation but lists aspects that should be taken into consideration:

- available time (years, decades?)

- available space (meters, kilometers?)

Table 5.   The Information and Necessity that this Information is Needed to Apply a Hydrogeological Model to Describe the Future Behavior of the Plume

| What is the behavior of the plume ?	Necessity
A characterization of soil composition and layers	+++
B groundwater flow direction and velocity	+++
C amount of contaminant in the plume	+++
What is the sustainability of the process ?	
D amount of metabolites in the plume	+++
E degradation rate	++
F characterization of solid phase	+
G characterization of carbon source ("fuel")	++
H characterization of redox conditions	++
I characterization of source	+
J more detailed groundwater sampling	+
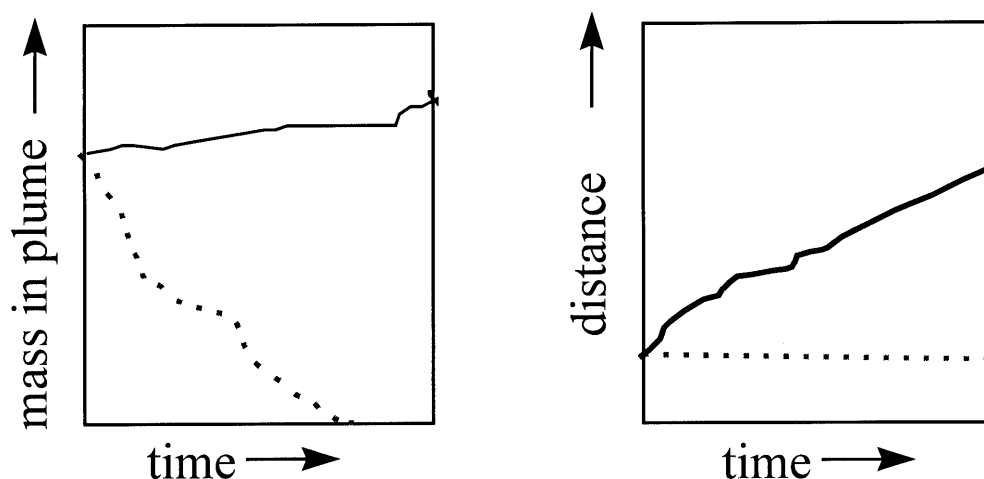
Figure 4.   Possible scenarios for the development of the load in the plume (A) and the spatial behavior of the plume (B)

- possibilities for other remedial strategies (costs, efficacy ?)

- juridical aspects (liability?)

- public opinion (cooperative or suspicious?)

Fourth Traffic Light: Prepare a Long-term Monitoring Plan

At the fourth traffic light the actual decision has been taken to implement MNA as remedial strategy. A long-term monitoring plan has to be designed to evaluate the model used and the efficacy of MNA,!and to make sure that surrounding targets are protected. This last aspect is achieved by positioning extra monitoring wells between plume and target. The position of these early alert wells is chosen in a way that when the contaminant should reach the early alert well, ample time is left to take additional measures.

The length of the implementation period depends on the appointments made at the third traffic light. After the implementation period the decision can be taken to stop the monitoring because the MNA process has proven to be reliable (green traffic light), or to extend the implementation period (orange) or to take additional measures (red).

Perspectives

The first experiences in the Netherlands are good because the DSS helps to collect and structure the site data in a uniform way. In addition, the DSS is a good communication tool that structures the discussion between authorities and site owners. In the second phase of the NOBIS project on MNA, some sites are deliberately being investigated where it is likely that the efficiacy of MNA will be insufficient. At these sites we expect orange and even red traffic lights. The goal is to make sure that at those locations where MNA is not a reliable option, the DSS will indicate so in an early stage.

References

Sinke, A.J.C., T.J. Heimovaara, H. Tonnaer, and H.J. van Veen. 1998. *Decision support model natural attenuation.* CUR-
NOBIS report 97-1-02 (in Dutch, with English summary).

Vegter, J.J. (this issue) Soil Cleanup policy and Monitored Natural Attenuation in the Netherlands

Natural Attenuation in the Federal Republic of Germany Background, Trends and Current Situation (B.A. Szelinksi, Ministry for the Environment, Germany)

1. Background and Legal Framework

The *phenomenon* of natural attenuation (NA) is well known for already almost 50 years. The first publications discussing this phenomenon in Germany date back to 1969[1]. Discussing natural attenuation is therefore neither new or revolutionary. It is actually amazing that it took so long until a broad discussion on how the phenomenon of natural attenuation can be used as a tool for remediation. In fact, the discussion in Germany outside the academic world has just started, and I will try to explain why.

Soil protection and the remediation of environmental contamination in soils and water is a rather newly developed area in Germany. Not that it has been unknown that pollution follows pathways, but methods to deal with remediation were underdeveloped and analytical tools were less precise. The belief in natural processes, i.e. in natural attenuation, was greater in the past as a result of a lack of knowledge about complex ecosystems and the behavior of pollutants in the environment and an underlying expectation that "nature will help itself". The whole development of this field only started in the late seventies when incidents with hazardous waste dumping and their full impact on the environment and the related public hazards alarmed the public. Quite clearly, nature does not help itself to the extent necessary to digest all man-made stress factors.

In Germany federal legislation on soil protection has been enacted only recently[2]. Prior to this new piece of legislation there was no *federal* basis to act in this field. It was quite clearly the domain of the federal states. How to deal with contaminated sites and contaminated soil was mainly regarded as a problem of water protection (groundwater and surface waters) since soil, as compared to air or water, did not have a special status as a protected medium under *environmental* laws and regulations. It may be argued that monitored natural attenuation (MNA) always had its specific field of application under water management aspects. This is quite true. But it is a fact that MNA never gained importance as an *accepted tool* for remediation of ground water pollution in Germany. This may have something to do with the outstanding status of groundwater protection in Germany, but also with the fact that in cases where other methods could not be applied for groundwater remediation, natural attenuation just happened without having the blessings of a remediation tool recognized by environmental law. It was - if at all - passively used or rather taken as granted and it was rarely monitored so that it is difficult now to draw from experiences of the past.

The FSPA which only came into force on March 1st, 1999, now gives a legal frame for soil management in general. It also includes regulations on the remediation of contaminated soil.

According to the German Soil Protection Act, the term remediation covers

• measures to eliminate or reduce pollution (decontamination measures) and

• measures to prevent or reduce the spreading of pollutants in a lasting way, without eliminating the pollutants themselves (containment measures)

This definition will be also applicable for measures under the relevant water acts since this is the only definition of remediation in the German legal system.

According to this definition MNA quite clearly is not a method for oil or groundwater decontamination but rather a safeguarding method which has at least to reach one goal: To prevent damage from spreading

Details on how remediation should take place are not regulated by the law itself but open to be dealt with by administrative ordinances which are preparedas needed. These ordinances will set values beyond which an investigation of the soil has to be carried out (Prüfwerte trigger values Art. 8 No. 1). Values beyond which remediation measures are obligatory will also be set by ordinance (Maßnahmenwerte action values Art 8 No. 2). Finally, ordinances can regulate the requirements for the remediation of contaminated soils, in particular the establishment of remediation goals, i.e. the extent to which measures to decontaminate or to encapsulate soils are necessary to avoid the spreading of contamination on a long-term basis (Art. 8 No. 3). It can already be underlined here that MNA, if and when it would become part of official remediation policy, may have a specific importance for the setting of remediation goals. MNA may allow certain

levels of residual pollution at contaminated sites which would be subject to monitored "passive remediation" as time goes by. This would be one of the most important benefits of a broader application which would generate relevant information through intensive monitoring.

As regards groundwater contamination, there is a competition in law between the FSPA and the relevant water legislation. The latter lies within the competence of the federal states. This does not make the implementation of natural attenuation any more simple. Any system which will implement natural attenuation will have to be aligned with the principles of groundwater protection provided by the Federal Water Act and the relevant state legislation. Here old and strong principles applythat do not allow any contamination whether the water source is used or not. This puts a limitation to an exposure pathways approach which accepts the exposure pathway to the groundwater just looking at the dilution of pollutants as a method to reduce contamination. It is very likely that for this reason special attention will have to be given to methods to arrive at mass balances and to the quality of modeling before MNA could be accepted.

Since MNA has its focus mainly on groundwater remediation which may or may not be connected to soil pollution the implementation of MNA as a remediation tool would require the approval of the federal states which may not be easy to get.

This is the legal background within which MNA can be considered in Germany.

As shown, German laws and regulations do not explicitly address MNA. They quite clearly would not prohibit the use of MNA. In fact, MNA could be addressed by the ordinances currently prepared under the Soil Protection Act. Such regulations, however, can only be applied for soil remediation. Remediation of the saturated zone (groundwater remediation) will follow a different legal system and different procedures. It will require an agreement with the federal states to establish principles for the use of MNA for groundwater remediation. The process of discussion between the federal government and the states has not started yet.

Since experiences using this tool for dealing with the remediation of contaminated soil and groundwater are - for the reasons mentioned above -very limited, more information is necessary before getting the process of implementation of MNA going.

2. Policy and Trends

Germany has so far been very reluctant to base its official policy on an approach which accepts intrinsic remediation by natural attenuation as an established method for remediation of contaminated soil or groundwater. There are multiple reasons for this reluctance. First of all, there are legal or quasi legal constraints and there was no federal legislation in the past. Remediation had to follow lists of contaminants as part of guidance documents issued by the federal states (comparable with the former "Dutch list") giving contamination levels which were used as action values and/or remediation values. At present the whole German system of soil protection is not designed to allow individual case-to-case decisions accepting a certain level of pollution and a time frame to allow for its degradation. It requires therefore a great deal of courage by the persons acting for the regional governments responsible for clean-up operations to disregard these values although it may be a case which could be solved by MNA. Following the list values is also the safer way also with regard to reactions from the interested public. In other words, it is safer not to do anything, or to follow established remediation guidelines, than to open a discussion on MNA in an individual case.

While there is no fixed German policy on the use of MNA as a means for soil or groundwater remediation, the legal system is open to it within the marginal conditions fixed in other laws and regulations or by general principles of law. It has to be said, however, that MNA will only develop as a means of soil and groundwater remediation if its principles will be documented at least in "guidelines", preferably at the federal level.

There is also a general trend to a broader use of MNA as a result of experiences with traditional "engineered" remediation.

The bad experience with traditional ways to deal with groundwater pollution from soil contamination has encouraged discussion into the prospects of the use of MNA,not only the often prohibitive costs of "technical" soil and groundwater remediation, but also because it is often an inefficient method that does not guarantee success and leaves open questions as to the cost-benefit relation of such activities. It has to be born in mind that engineered remediation of contaminated sites in the past was generally only used in very serious cases where there was significant risk for man and/or the environment. Without being outspoken there is a general trend to leave contaminated sites untouched when there is neither an acute threat for recipients through exposure pathways nor a need for remediation as prerequisite to future uses of the land in question. This situation is unsatisfactory since there is generally only a cursory (initial) risk assessment for these sites and there generally is only limited monitoring done which gives neither an accurate picture of the risks involved nor does it make it possible to assess the grade to which NA takes place and could be used. This also underlines the necessity to know more about the natural processes taking place and their impact on contaminants in

general. It is therefore expected that MNA will be a good tool to be used at sites for which engineered remediation is not a promising option and where safety can be substantially improved by proper monitoring. The establishment of tools to monitor natural attenuation would help deal with a larger number of contaminated sites, if monitoring can be done at reasonable cost.

It has to be said, however, that such an approach will also carry some dangers, particularly when mere dilution would be accepted as "natural attenuation" and if the use of MNA would lead to a more negligent behavior accepting certain levels of pollution. These dangers can be minimized if MNA would be limited to already existing contamination.

On the policy level the Federal Ministry for the Environment has started to look more closely at the pros and cons of MNA with regard to former military sites. With the withdrawal of the Soviet troops from Eastern Germany, a large number of military lands and/or facilities was returned to the federal government, often in a very bad condition as regards soil and groundwater contamination particularly with mineral oil products including chlorinated hydrocarbons. Since expenditure was already extremely high as result of the reunification process, only a limited number of cases underwent active remediation beyond the level of immediate measures.

Military sites are particularly promising for the use of MNA for multiple reasons:

- Very often military sites are "out in the middle of nowhere" without clear pathways to recipients for the pollutants in question,

- Most of these sites are far away from competitive uses,

- Very often pollution is clearly located and easy to control,

- There is generally only a limited number of pollutants in question of which hydrocarbons are the most prominent. The contamination is generally straightforward and simple.

Since military sites can be regarded as good candidates to assess the potential for MNA, a number of research projects have been launched to assess the potential for MNA for such sites.

There are no fixed criteria developed yet. However, a guidance document for the use of MNA will be prepared soon and will establish a number of criteria as prerequisites for the use of MNA, such as:

- There must be favorable geological conditions

- The source of contamination should be stable/eliminated

- The plume has to be assessed and has to be in a stable condition

- The pollutants must in principle be biodegradable

- A proper monitoring system with regular sampling following given procedures must be established

- There must be no danger of pollution spreading to possible recipients

The next step to be taken will be the development of a methodology to make use of MNA in practice.

3.   Research Activities

In the last few years some research has been carried out to prepare for the ordinances under the FSPA to evaluate the possibilities and goals of guidelines on NMA.

3.1.   *Mobility, Transfer and Degradation Behavior of Pollutants Found at Contaminated Military Sites*

Assessment of the groundwater established the pollution potential of 54 substances. These substances include hydrocarbons, halogenated hydrocarbons (solvents), polycyclic hydrocarbons (aromates), explosives and chemical warfare agents.

Data for the transfer and degradation behavior were put in relation to ecotoxicological and humanotoxicological properties of the substances. Threshold values for the substances with regard to groundwater protection will be proposed as well as "no effect values". A simulation model to assess the mobility and transfer of the pollutants investigated by the study will be presented. The final Report is expected in summer 1999.

3.2.   Decision Base on Safeguarding and Remediation at Military Tank Farms

First investigations on the degradation and migration of mineral oils and mineral oil products, aromatics and chlorinated hydrocarbons in soil and groundwater were carried out between 1992 and 1997 at a former Soviet military tank farm. Laboratory and pilot scale research aimed at: assessing the potential for NA, characterizing the factors relevant for NA, determining the effectiveness of stimulating NA by means of nutrients, elaborating the respective mass balances and developing a cost-effective microbiological remediation method for soil contaminated with mineral oil products.

3.3 Decision Base for Safeguarding and Remediation Concepts at Military Tank Farms

In a theoretical research project an assessment of the risk potential at 8 military tank farms was done in an attempt to establish criteria for risk based concepts for the remediation of such sites. This project which is still ongoing will also discuss the international state of the art, in particular US experiences, and their adaptability to German conditions. The results of this project confirmed in principle that MNA is a viable tool to deal with pollution by mineral oil products, which often produce rather stable, shrinking plumes in relatively short periods of time. This project, however, did not look at the impact of additives in fuels which can be problematic.

3.4.   Long-term Investigation on the Possibilities and Limits of the Use of MNA for Certain Contaminants at Military Sites

The study will investigate possibilities and limitations of the use of MNA also as a supportive tool to remediate contaminated military sites. The findings of this study will be quantified according to a work program establishing a scheme to differentiate between losses (emissions) and actual reduction of certain pollutants resulting in a mass balance.

As result, a set of tools shall be elaborated that will determine the clean-up rate in relation to time, certain hydrogeological and other conditions, and show the potential for a generalized evaluation scheme for practical use. To this end, the relevance of site specific data as data on geology, hydrogeology, soil quality, soil biology and on other soil properties and on meteorology, will be investigated and evaluated to establish a model monitoring program to assess transport and reaction processes in seepage and groundwater.

The aim of this project is to determine the relevant factors for a scheme for monitored natural attenuation which can be used in a multitude of practical cases.

4.   Actual Conditions to Allow for MNA in Remediation

Technical guidelines or established scientific criteria for the remediation of soil and/or groundwater are not yet available in Germany on the federal level. Existing state rules also do not address technical details. MNA can therefore only be applied on a case-to-case basis and after individual site assessment. Requirements would then be fixed within the remediation plan if required according to Art. 14 Federal Soil Protection Act (FSPA) or by means of a remediation order under water laws, respectively.

As mentioned above, nothing strictly hinders the use of MNA. The whole administrative and institutional framework is already in place to supervise and implement MNA and to provide for any contingencies during the process. All decisions which may be necessary could be part of a remediation plan under the soil protection act or a remediation order under water laws. Only guidance on the aspects to be considered using MNA is lacking in the administrative system. This is particularly true for the following aspects:

- Specific contaminants or classes of contaminants for which MNA in principle can be used (currently there is no listing available for which contaminants MNA can be applied)

- Site characterization, monitoring and modeling (although a site characterization is generally made as a first step to assess contaminated sites, it does not necessarily and automatically look at all parameters necessary to make a decision on the use of MNA)

Besides there is no sufficient operating history available in Germany to allow the use of the *phenomenon* as a method. The scientific evidence on the mechanisms is still regarded as insufficient to allow straightforward legislation. Therefore the currently ongoing work on regulations under the soil protection act disregards the knowledge internationally available on MNA.

5.   Outlook

What will be the steps regarding the implementation of MNA to be taken in the near future in Germany? The Federal Environmental Agency is presentlyu looking into the possibility to issue a preliminary guideline for the use of MNA in practical remediation cases. It is quite clear that a number of principles regarding MNA can be regarded as being safe although there is no experience with particular cases.

General principles regarding the suitability of MNA can be elaborated in the form of a negative/positive catalogue listing the criteria under which MNA can be regarded as a workable tool for remediation and - which is more important - listing the criteria under which MNA cannot be used according to available knowledge and legal restrictions.

Such a list may also give indication as to the type of contaminants and contamination for which MNA is suitable in principle. Quite clearly this would first be mineral oils and mineral oil derived products and their contaminats and some other organic contaminants. Existing knowledge has to be evaluated. There is for example substantial information available on the long-term behavior of explosives and warfare related agents which should allow an assessment of the use of MNA. This would open a broad field of application of the tool of natural attenuation and generate additional knowledge and experience as the result of long-term monitoring efforts.

Additionally the aspects of the monitoring part for MNA can be regulated on the basis of sufficient knowledge on soil and groundwater monitoring (distribution of monitoring wells, sampling etc.)

6.   Conclusions

The use of MNA may be a substantial contribution to the tools used for remediation of soil and groundwater pollution, either alone or in combination with other methods of remediation, in particular of microbiological treatment.

MNA may have particular benefits in cases where an engineered remediation is not technically or economically feasible. Particularly the better cost-benefit ratio as compared to treatment methods is a strong incentive to make use of this tool. The use of MNA also looks very promising to find a limitation of otherwise "endless pump and treat remediation" in terms of taking MNA into consideration for setting remediation goals.

To make the best use of this method, it will be necessary to have better knowledge of the long- term behavior of pollutants which are accessible for MNA and of the influence of transport media conditions.

The use of MNA will also require an agreement of pollutant transfer modelling since this is the weakest point in the system, but of great relevance when it comes to public acceptance.

MNA should be used with care according to the development of the available knowledge on the underlying processes and cannot be regarded as a "multi-purpose-wonder-tool" for the remediation of contaminated sites.

Due consideration should also be given to the polluter-pays principle in case there is a great cost benefit when MNA is used as compared to engineered remediation. It may not be acceptable that the use of MNA gives the polluter a cost advantage using "public goods" like soil and groundwater.

All activities using natural attenuation to a greater extent in the future will have to look at public acceptance, which may well be a crucial factor in many countries. People have been told too long that nature can help itself. The limits of natural processes are known to the public. The use of MNA as a tool for remedial action will - at least in Germany - require convincing evidence that it works in practice along with an open information policy on the tools used for making a remediation plan based on MNA, on monitoring the process, and on alternative actions in case of contingencies.

Controlled Reactive Zones (CORZO): The Implementation of Innovative Plume Control Techniques for Groundwater Protection at Contaminated Sites. (Georg Teutsch, University of Tübingen, Germany)

1. Plume vs. Source

Today most experts agree that clean-up of contaminant source zones is hardly achievable at reasonable costs [Travis and Doty, 1990]. This is specifically true for industrial sites where non-aqueous phase liquids (NAPL) like petroleum hydrocarbons, chlorinated solvents or tar-oil have penetrated into the ground (Figure 1). As a consequence, concepts which focus on the control of the groundwater plume rather than the elimination of the source have received increasing attention during recent years [e.g. Christensen, 1994; Borden et al., 1995]. For compounds which are sufficiently biodegradable, *natural attenuation* can be a valid concept [Wiedemeier et al., 1995 and 1999; Rifai et al., 1995; US-EPA OSWER, 1999], whereas man-made *reactive barriers* [Teutsch et al., 1997; Gillham and Hannesin, 1992] are needed in cases where the natural attenuation leads to an unacceptably long aquifer reactive zone. Most likely, appropriate combinations of both concepts may lead to very cost-effective groundwater protection measures specifically suitable to large industrial areas, where the source zones are often poorly defined or hardly accessible.

However, site-specific field measurement and modelling techniques are still lacking for *the implementation* of these new approaches. These should allow a reliable field scale quantification of the contaminant source strength as well as the characterisation of the contaminant plume with respect to retardation, dilution and degradation.

The objective of the project **C**ontrolled **R**eactive **Zo**nes (CORZO) is to develop and demonstrate at selected field sites new plume control and monitoring concepts which integrate innovative field techniques for the direct measurement of contaminant fluxes with stochastic transport modelling approaches based on control-planes. This has certain advantages (PROS) but also some disadvantages (CONS):
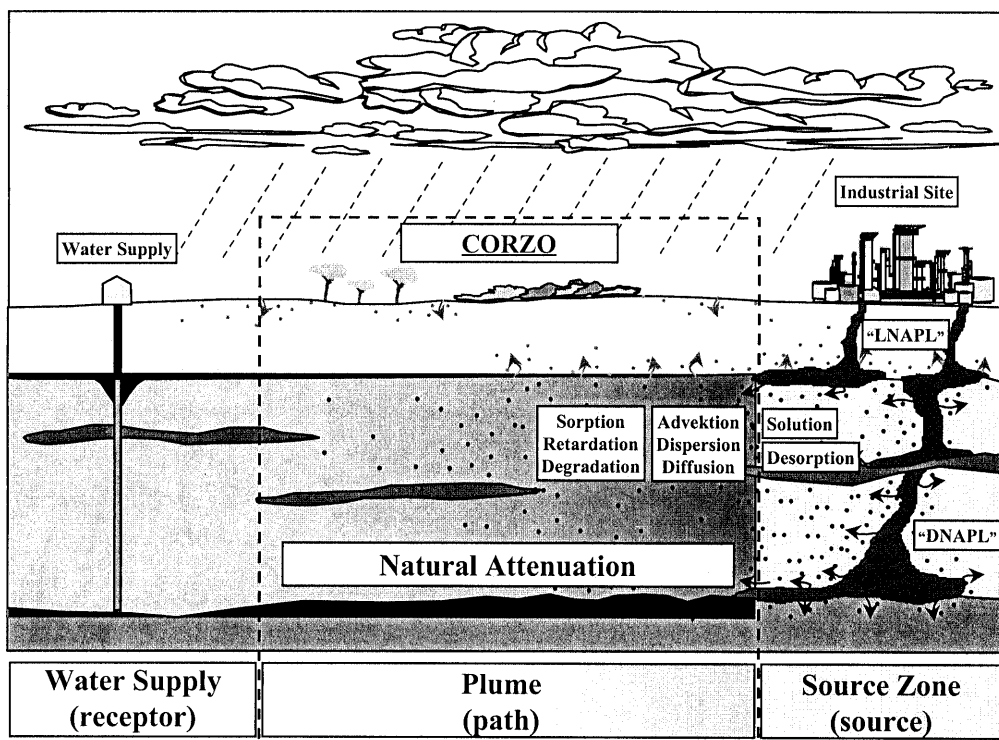

Figure 1.   Typical scenario at industrial contaminated sites: The CORZO approach focuses on the control of groundwater *plumes* rather than the clean-up of *source zones*.

Pros

- Source zone investigations not required

- Accessibility of the source zone not limiting

- Complex source zone release (emission) mechanisms need not be quantified for risk assessment

- Groundwater plumes show often low concentrations/fluxes

- Inefficient source zone clean-up can be avoided

- Natural attenuation concept applicable to plumes

- Plume control decision independent of source-zone management

- Cost-efficient plume control/clean-up techniques (e.g. reactive barriers) applicable

Cons

- Source zone emission may last very long

- Restricted (future) land use in source zone

- Limited acceptance by regulators

- Field scale quantification of contaminant fate and transport still a research issue

2.   The Problem of Contaminated Site Evaluation

2.1.   *Source Strength Characterisation*

Today the most common approach to source strength characterisation is based on soil and groundwater samples which are obtained from boreholes, ditches, piles etc (Figure 2). However, practical experience shows that these types of approaches generally fail to produce reliable results due to (a) the difficulty of changes calculating or measuring relevant, compound specific emission rates (mass/time) from contaminated samples, (b) the lack of an adequate data-density to produce reliable (regionalised) site-scale emission estimates from point measurements and (c) the lack of field scale methods for the quantification of the fate and transport of contaminants.

Recently presented statistics of contaminated sites investigated in S-Germany indicates that 3 out of 4 hazardous waste sites did in fact not lead to a significant deterioration of the downstream groundwater quality. However, there was no direct way of predicting up-front with a reasonable level of certainty which of the sites would lead to the high-contaminant release rates.

2.2.   *Contaminant Plume Characterisation*

Transport mechanisms controlling the contaminant propagation in the subsurface are commonly estimated from groundwater samples obtained at various distances downstream of the source zone. However, bearing in mind that both the contaminant distribution and the hydraulic properties (hence, the water fluxes) can be extremely heterogeneous within an industrial area (source zone), point concentration measurements are not likely to provide a representative estimate of the groundwater quality at a site. Various experiences from well-instrumented groundwater research field sites indicate that tracking a groundwater plume which develops out of a well-controlled release zone is hard to achieve in practice [Ptak et al., 1996]. Consequently, the simple question whether an observed concentration decrease (e.g. of an organic contaminant) in downstream direction is caused by dilution or degradation would require a large number of boreholes in order to reconstruct the three-dimensional contaminant distribution. This approach is therefore not practical for standard field sites.

2.2.1.   Contaminants in Groundwater

Based on surveys conducted in the USA and Germany, the groundwater contaminants most frequently found in groundwater plumes are *chlorinated hydrocarbons* (CHC), *BTEX-compounds* and *chlorobenzenes* (Figure 3).

2.2.2.   Plume Length Statistics

In a recently conducted survey by the Chair of Applied Geology in Tübingen [Schiedek et al., 1997], the travel distances of 256 published groundwater plumes were analysed. It is seen that the observed plume lengths differ considerably for the different (organic) compounds (Figure 4).
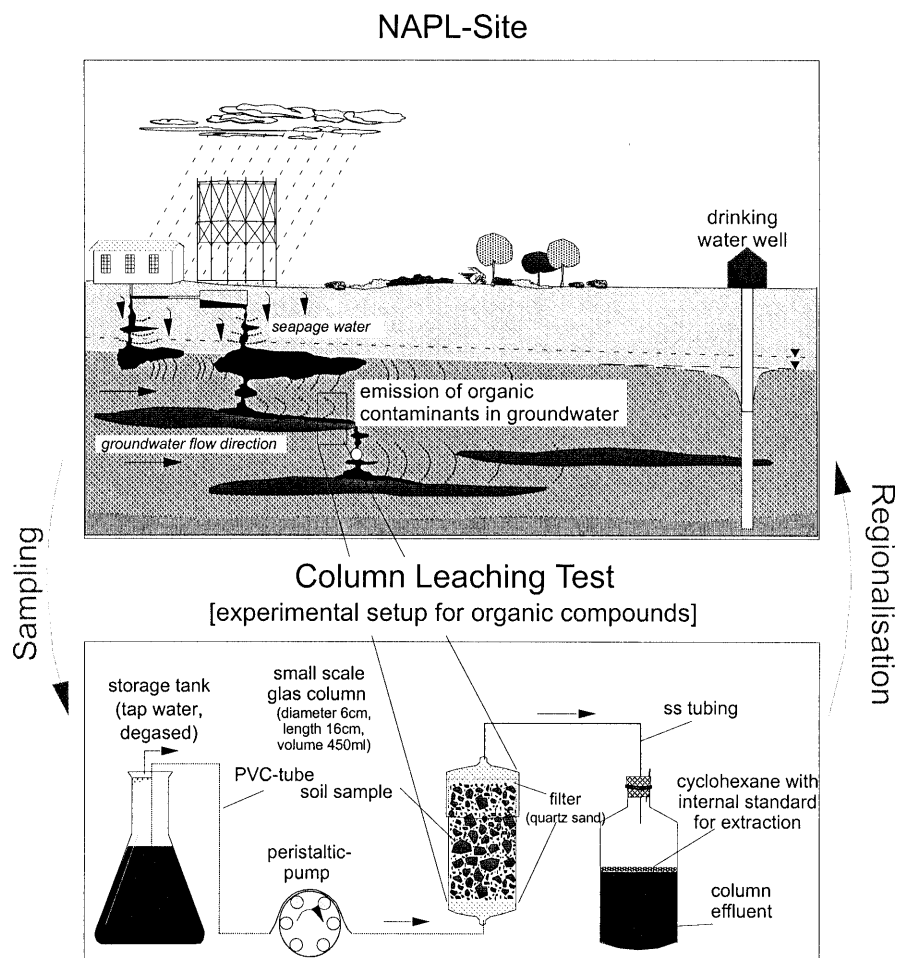
NAPL-Site

Column Leaching Test
[experimental setup for organic compounds]

Figure 2. The emission from a contaminated site (location, size and strength of source) is commonly performed on the basis of *soil sampling* and *leaching tests*. Even though the leaching test procedures are being improved considerably and also standardised, the regionalisation of the test results is considered highly uncertain.
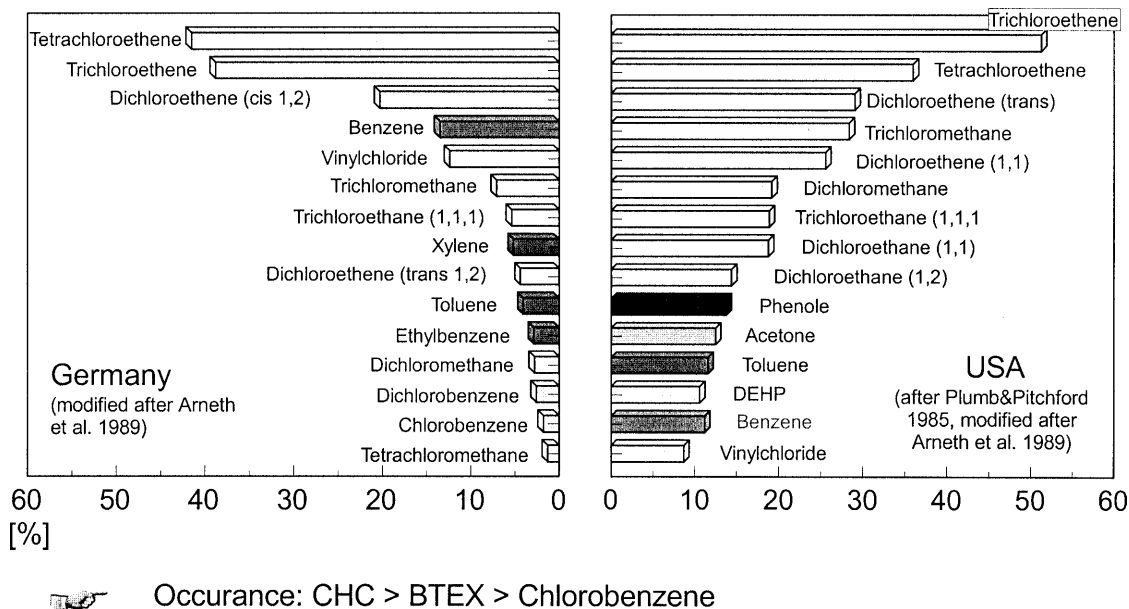

Germany
(modified after Arneth et al. 1989)

USA
(after Plumb&Pitchford 1985, modified after Arneth et al. 1989)

☞ Occurance: CHC > BTEX > Chlorobenzene

Figure 3. Groundwater contaminants most frequently found in groundwater plumes.
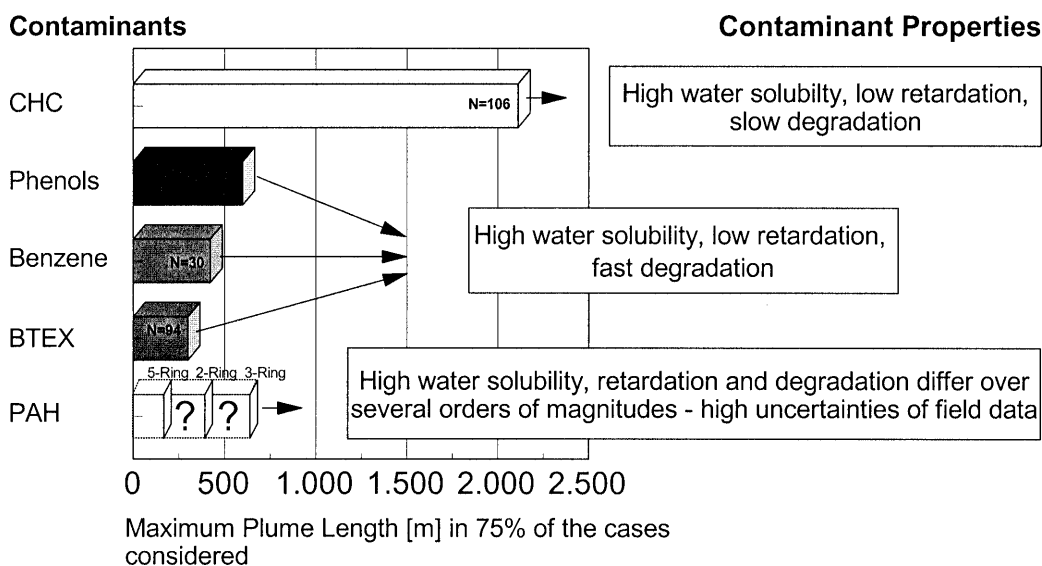
Figure 4.   Typical plume length for different contaminants: Natural attenuation is effective for all (organic) compounds but quantification requires site-specific data.

2.2.3.   Quantification at Field Scale

Computer simulations of a NAPL-spill in heterogeneous Media [Whittaker et al., 1998] have shown that under natural conditions the heterogeneous structure of the subsurface leads to extremely complex NAPL distribution in the *source zone* and therefore to extremely complex groundwater *plumes.* Consequently, *point-concentration measurements* in the groundwater plume might be highly erratic.

Besides the uncertainties caused by the unknown NAPL-distribution within the *source zone* and the complexity of the *plume*, the uncertainty about the location of the *point sources* is considered most significant (Figure 5).

3.   The New Approach

3.1.   Conceptual Model

In order to overcome the limitations of the source zone and plume characterisation described above, the new site evaluation concept aims at quantifying the entire contaminant mass flux across given control planes (Figure 6) rather than the spatial distribution of point concentrations. Conceptually, this leads directly to the relevant issues of quantifying source strengths as well as plume strengths, e.g. providing a way of directly proving the occurrence of *natural attenuation* in case the total contaminant flux (not the concentration !) decreases with distance from the source [Ptak et al., 1998; Teutsch et al., 1999].

Based on some recently developed field techniques, the mass flux can directly be determined across the entire plume using pumping wells and a numerically based inversion of the observed time-concentration curves [Schwarz et al., 1998 and Holder et al., 1998]. In fact, these curves also contain information about spatial heterogeneity, so that they are matched by a non-point stochastic modelling concept which will be used to interpret the flux measurements in terms of site specific effective transport parameters [Dagan and Cvetkovic, 1996; Cvetkovic and Dagan, 1996]. The effective transport parameters represent a spatial integral of the local parameter values which cannot be directly measured in the field. Moreover, comparing these curves for different reactive contaminants also helps in quantifying natural degradation processes. The technique can conveniently be coupled to measurements of redox-sensitive parameters, and degradation products from the organic chemicals in order to provide further information on the degradation process in the aquifer.

Based on this coupled measurement-modelling approach, predictions of the expected plume propagation can be performed [Herfort et al., 1999] and (cost-) optimal solutions to control the plume can be developed. In case a *natural attenuation* solution is chosen, these tools will allow the development of appropriate strategies for risk-based contaminated land management including efficient monitoring concepts. If a *reactive barrier* solution is preferable, the average contaminant load reaching the reactive barrier can be calculated allowing for a safe and still (cost-) optimal design of the reactive material.
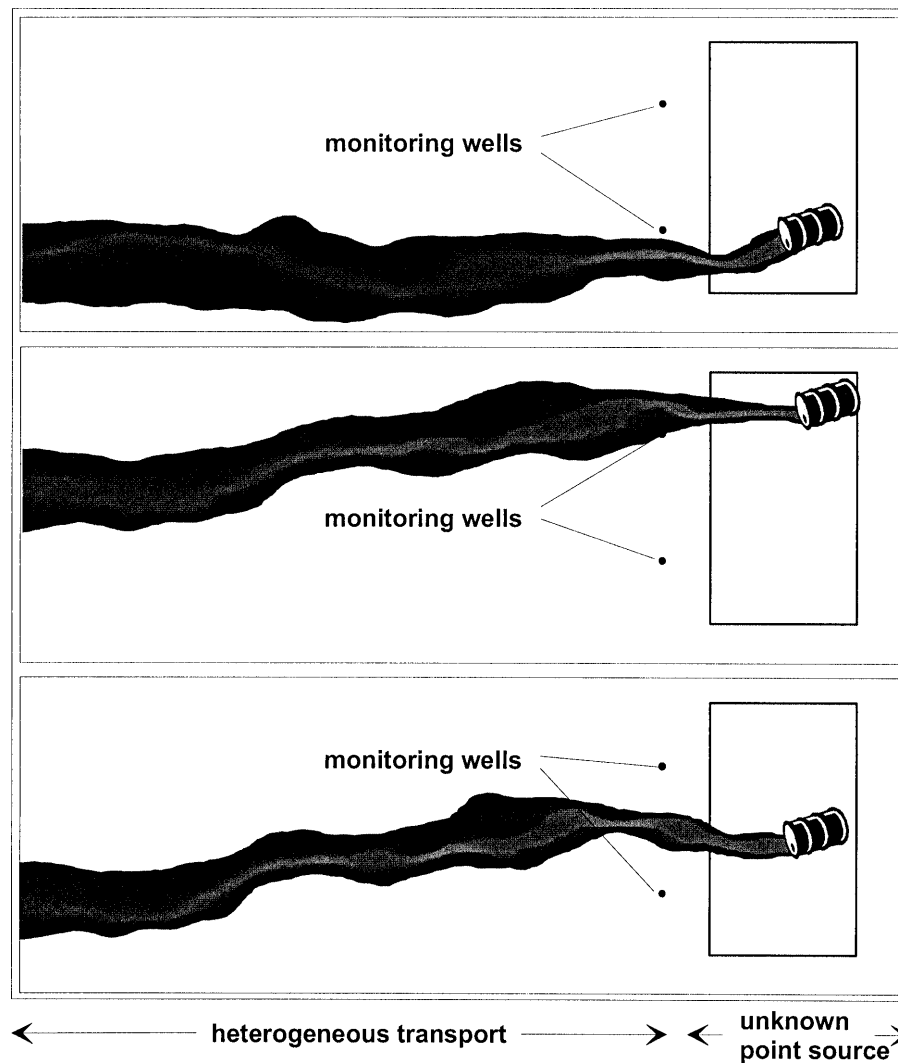
Figure 5. Detectability of point sources under field scale conditions is very difficult: Common groundwater monitoring techniques are likely to either over- or underestimate the contamination.

The new immission approach yields *average* values of concentration and flux at the relevant site scale. It leads to a realistic assessment of contaminant risk because it is not affected by locally occurring peak values. This has certain advantages (PROS) but also some disadvantages (CONS):

PROS

• Extensive soil sampling and leaching tests not required

• Regionalisation of point-measurements not required

• Quantification of mass transfer mechanisms in the source zone not required

• Not affected by (point-) source location uncertainty

• Regulators appreciate high degree of certainty

• *Natural attenuation* can be quantified/proven at field scale (mass-flux decrease !)

• Yields directly relevant data for model-based risk assessment at site scale
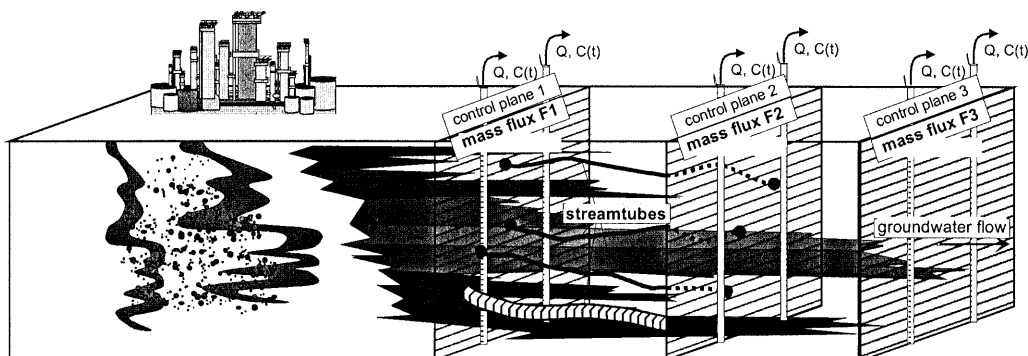
Figure 6. With the new site evaluation technique, rather than estimating the contaminant distribution based on point-concentrations, the entire contaminant mass flux (immission) across given control planes is quantified.

CONS

- Wells, pump-tests and chemical analysis required

- Research still required to validate the new technology under various field and contaminant conditions, including adequate modelling

3.2.   *Implementation (steady-state)*

The spatial averaging is obtained by pumping in one or more downstream wells and simultaneous observation of the concentration development through time. From that, the mean plume concentration as well as the flux under natural gradient can be back-calculated using various analytical (simple cases) and numerical (complex cases) inversion techniques [Schwarz et al., 1998 and Holder et al., 1998; Figure 7].

3.3.   *Demonstration at the Eppelheim-Site (unsteady-state)*

The new immission technique was evaluated at a well-instrumented demonstration site of the Landesanstalt fur Umweltschutz (LfU) - the state environmental protection agency - in Baden - Wurttemberg, Germany. The distribution of chlorinated hydrocarbons within the plume was reproduced across the control plane down to less than 1 micro-gram/litre (Figure 8).

4.   Expected Benefit

The expected benefits from the new concepts are: (a) the reduced site evaluation effort leading directly to emission rates relevant for regulatory purposes, (b) the reduced uncertainty of non-point measurements and estimates in comparison to soil and groundwater samples (point measurements), (c) the simplified modelling using spatially integrated (effective) transport parameters and (d) the direct relevance to subsequent plume control measures like natural attenuation and reactive barriers.

The final goal is to develop a reliable plume-oriented risk management tool-set. This is summarised in the decision-tree outlined in Figure 9.

E = $C_P Q_P$ C_{AV} = E / Q_A

E = total mass flux
C_P = contaminant concentration in the pumping well
Q_P = pumping rate
Q_A = natural groundwater flow through control plane
C_{AV} = mean contaminant concentration in groundwater
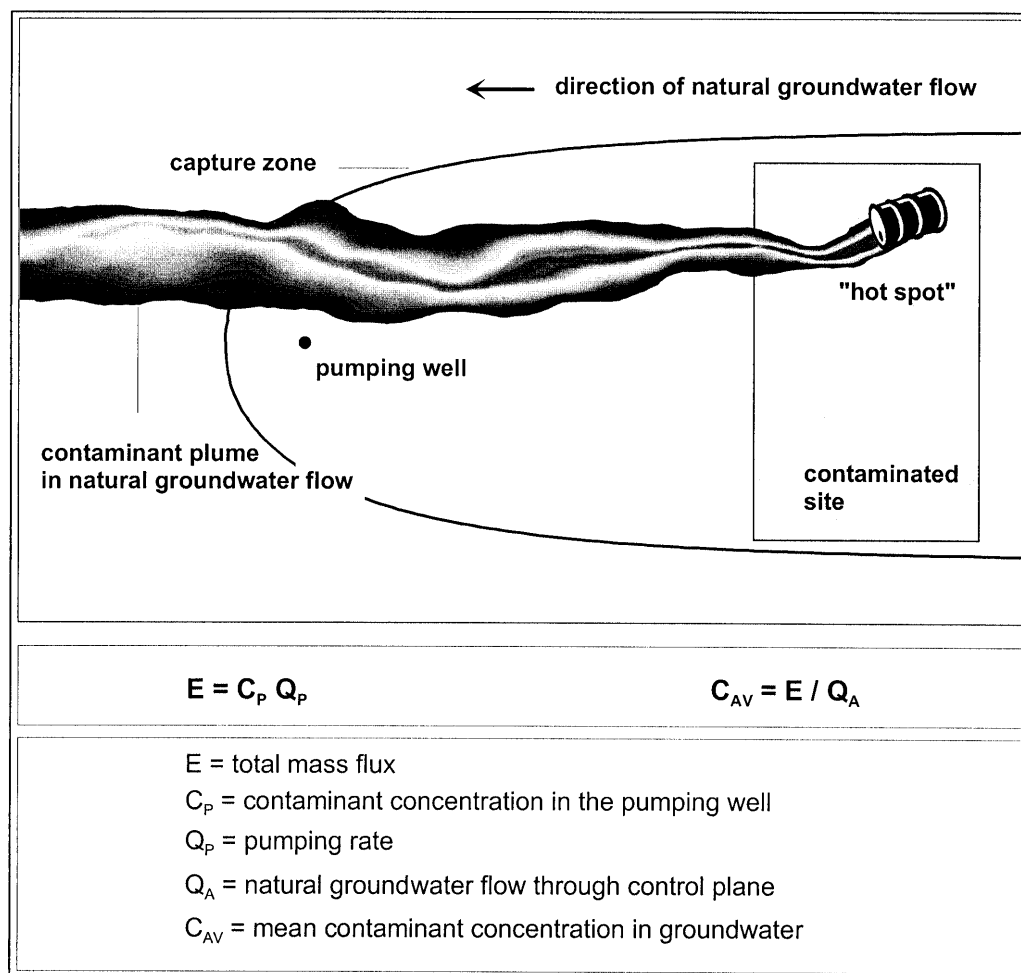
Figure 7.   Using the new immission approach, concentrations and fluxes are determined for the entire groundwater volume pumped at the well.

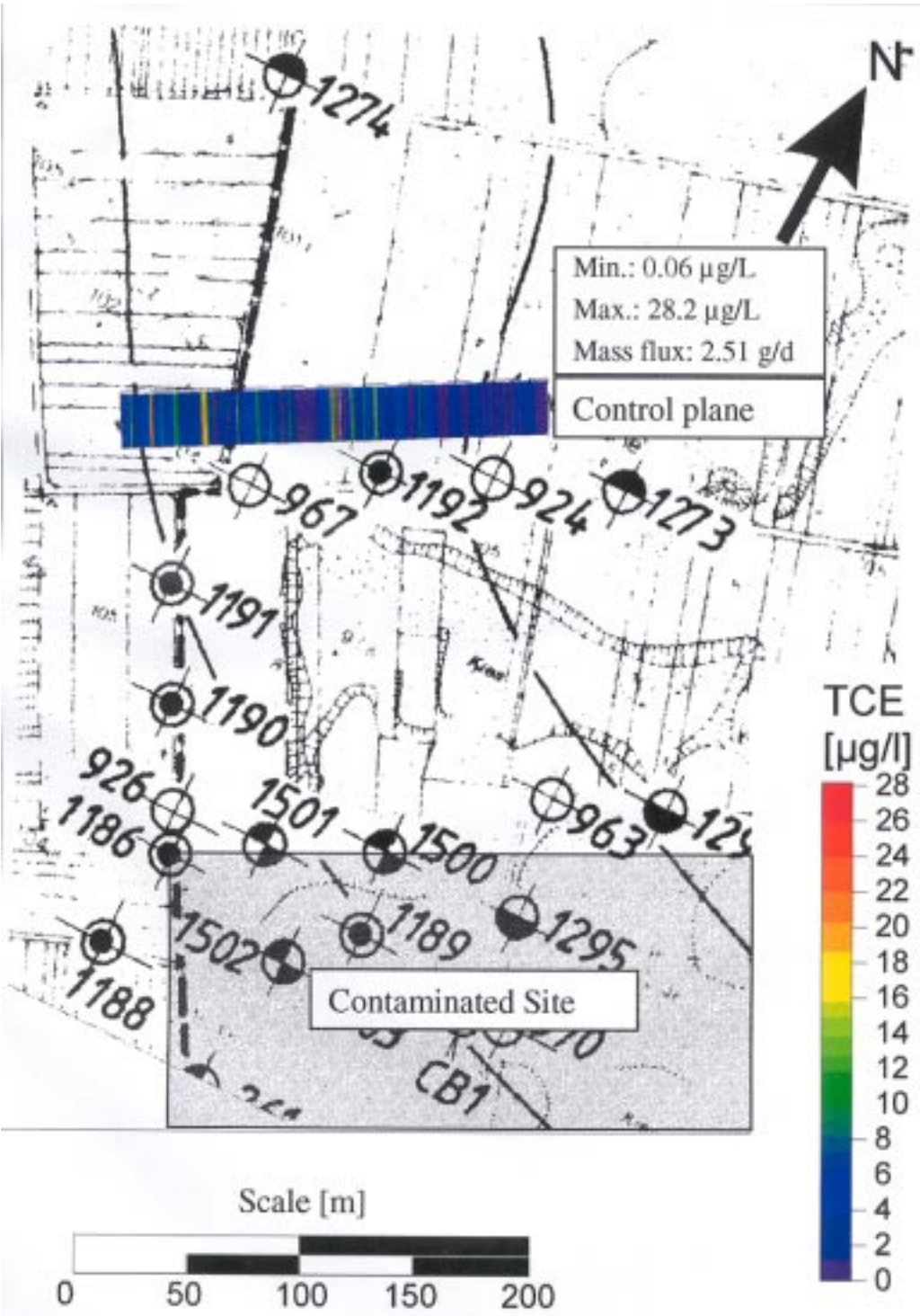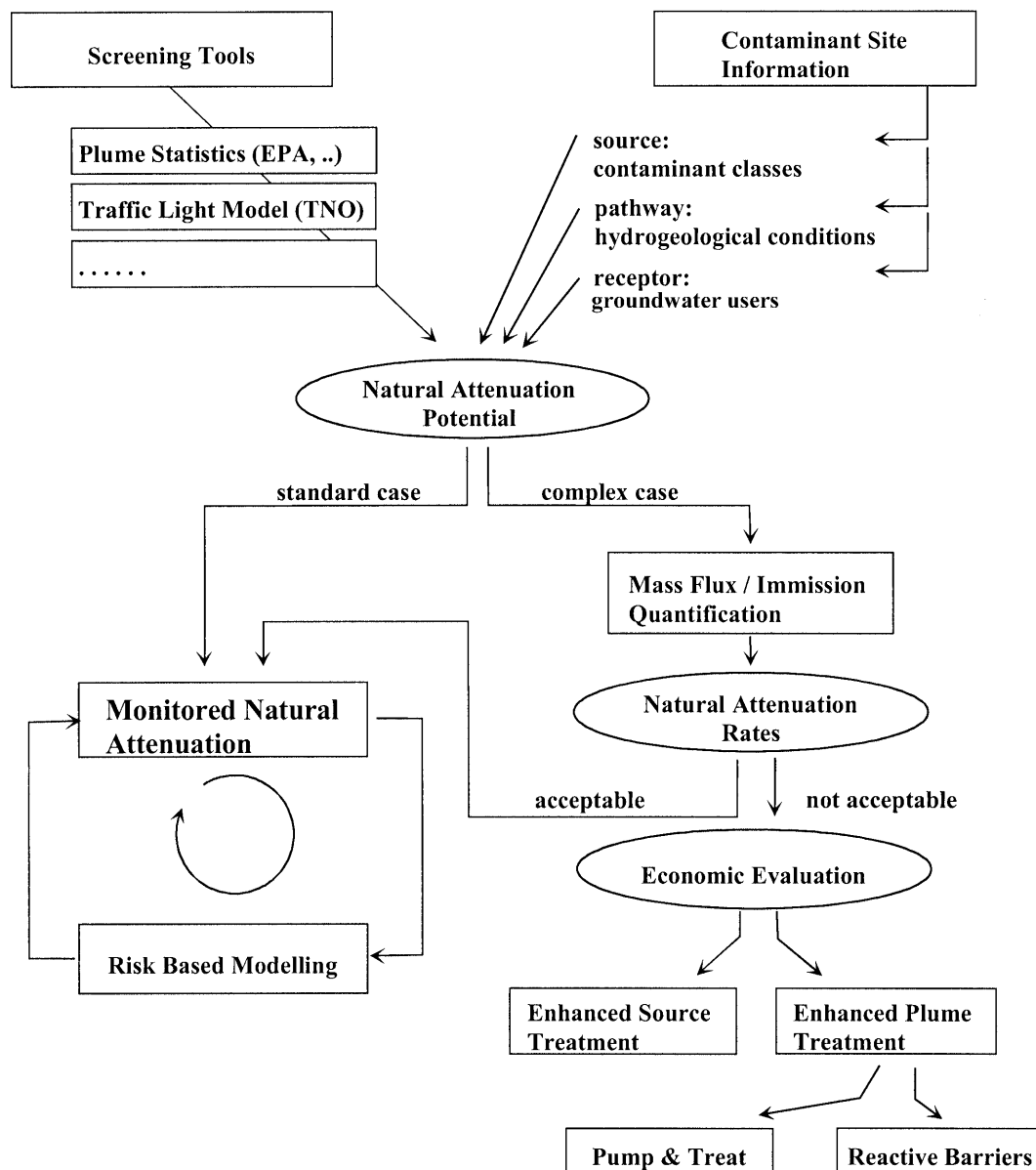**Figure 8.**

Figure 9.   Decision-tree for a plume oriented risk management.

5.   Literature

Arneth, J.D.; Milde, G.; Kerndorff, H.; Schleyer, R. (1989): Waste deposit influences on groundwater quality as a tool for waste type and site selection for final storage quality.- in: Baccini, P. (Hrsg.): The Landfill.- Lecture Notes in Earth Sciences, Vol. 20, Springer-Verlag, Berlin.

Borden, R. C.; Gomez, C. A.; Becker, M. T. (1995): Geochemical indicators of intrinsic bioremediation.- Ground Water , 33 (2): 180-189.

Christensen, T.H.; Kjeldsen, P.; Albrechtsen, H.-J.; Gorm, H.; Nielsen, P.H.; Bjerg, P.L.; Holm P.E. (1994): Attenuation of landfill leachate pollutants in aquifers.- Critical Reviews in Environmental Science and Technology, 24 (2): 119-202.

Cvetkovic, V. and Dagan, G. (1996): Reactive transport and immiscible flow in geological media. II Applications.- Proc. R. Soc. Lond., A 452, S. 303-328.Dagan, G. and Cvetkovic, V. (1996): Reactive transport and immiscible flow in geological media. I General theory.- Proc. R. Soc. Lond., A 452, S. 285-301.

Gillham, R.W. and Hannesin, O. (1992): Metal-catalysed abiotic degradation of halogenated organic compounds.- Proc. Of the IAH Conf. On Modern Trends in Hydrogeology, May 10-13: 94-103; Hamilton, Ontario.

Herfort, M., Ptak, T., Liedl, R. and Teutsch, G. (1999): A new approach for the investigation of natural attenuation at field scale. Proceedings of the 1999 Contaminated Site Remediation Conference, 21-25 March 1999, Fremantle, Australia.

Holder, T., Teutsch, G., Ptak, T. and Schwarz, R. (1998): A new approach for source zone characterization: The Neckar Valley study. In Groundwater Quality: Remediation and Protection, IAHS Publication No. 250, ISSN 0144-7815, 49-55.

LfU Baden-Württemberg / LAG Univ. of Tübingen, (1997): Demonstrationsprojekt zur technischen Erprobung eines neuen Erkundungskonzepts zur Untersuchung der Emission und Immission an Altlastenstandorten. Report LAG 01/0460, LfU Baden-Württemberg, Angewandte Geologie Tübingen.

Plumb, R.H. Jr. (1987): A comparison of ground water monitoring data from CERCLA and RCRA sites.- Ground Water Monitoring Review, 7 (4): 94-100.

Ptak, T., Schad, H., Hofmann, B., Teutsch, G. und Kobus, H. (1996): "Methoden zur Erkundung und zur Simulation von Strömung und Transport in heterogenen Aquiferen", Berichte Umweltforschung Baden-Württemberg, FZKA-PWAB 17, September 1996, ISSN 1432-167X, 152 S.

Ptak, T., Teutsch, G. and Schwarz, R. (1998): Grundwasser-Gefährdungsabschätzung durch Emissions- und Immissionsmessungen an Deponien und Altlasten: Numerische Untersuchungen zur Anwendung und Auswertung. Projekt Wasser-Abfall-Boden, Berichte Umweltforschung Baden-Württemberg, Forschungszentrum Karlsruhe.

Rifai, H.S.; Borden, R.C.; Wilson, J.T.; Ward, C.H. (1995): Intrinsic bioattenuation for subsurface restoration.- in: Hinchee, R.E.; Wilson, J.T.; Downey, D.C. Columbus (Hrsg.): 3. International In Situ and On-Site Bioreclamation Symposium, San Diego, CA/USA, 1995, 24.-27.Apr, Battelle Press. OH, USA 1995, Bd 3(1): 1-29.

Schiedek, T., Grathwohl, P. and Teutsch, G. (1997): Literaturstudie zum natürlichen Rückhalt / Abbau von Schadstoffen im Grundwasser. Report LAG 01/0460, LfU Baden-Württemberg, Angewandte Geologie Tübingen.

Schwarz, R., Ptak, T., Holder, H. und Teutsch, G. (1998): Groundwater risk assessment at contaminated sites: A new investigation approach. In Groundwater Quality: Remediation and Protection, IAHS Publication No. 250, ISSN 0144-7815, 68-71.

Teutsch, G., Grathwohl, P., Schad, H. and Werner, P. (1997): In-situ-Reaktionswände -ein neuer Ansatz zur passiven Sanierung von Boden- und Grundwasserverunreinigungen. Grundwasser, 1: 12-20.

Teutsch, G., Ptak, T., Schwarz, R. und Holder, T. (1999): "Ein neues Verfahren zur Quantifizierung der Grundwasserimmission: I. Theoretische Grundlagen", Grundwasser (submitted).

Travis, C.C.;Doty, C.B. (1990): Can contaminated aquifers at Superfund sites be remediated?- Environmental Science & Technology, 24 (10): 1464-1466.

US-EPA OSWER(1999): Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites. Directive 9200.4-17P.

Whittaker, J., Grathwohl, P., Teutsch, G. and Sudicky, E. (1998): Numerical simulations of the flow and transport of dense non aqueous phase liquids (DNAPLs) in naturally heterogeneous porous media. In Groundwater Quality: Remediation and Protection, IAHS Publication No. 250, ISSN 0144-7815, 190-193.

Wiedemeier, T.H., Rifai, H.S., Newell, C.J., Wilson, J.T. (1999): Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface. John Wiley and Sons, New York.

Wiedemeier, T.H.; Swanson, M.A.; Wilson, J.T.; Kampbell, D.H.; Miller, R.N.; Hansen, J.E. (1995): Patterns of intrinsic bioremediation at two U.S. Air Force Bases.- in: Hinchee, R.E.; Wilson, J.T.; Downey, D.C. Columbus (Hrsg.): 3. International In Situ and On-Site Bioreclamation Symposium, San Diego, CA/USA, 1995, 24.-27.Apr, Battelle Press. OH, USA 1995, Bd 3(1): 31-51.

Field Evidence of Ineffective Natural Attenuation of Phenolic Compounds in a Sandstone Aquifer

Field Evidence of Ineffective Natural Attenuation of Phenolic Compounds in a Sandstone Aquifer (Steven F. Thornton[1], Steven A. Banwart[1], David N. Lerner[1], Roger W. Pickup[2], Michael .J. Spence [3]and Geoff M. Williams[4])

Abstract

A combination of field data and theoretical approaches is used to assess the natural attenuation and status of a complex plume of phenolic compounds (phenol, cresols, xylenols) in a deep, consolidated, UK Permo-Triassic sandstone aquifer. Biodegradation of the phenolic compounds at concentrations up to 12,500mg l^{-1} is occurring under aerobic, NO_3-reducing, Mn/Fe-reducing, SO_4-reducing and methanogenic conditions in the aquifer, with the accumulation of inorganic and organic metabolites in the plume. An electron and carbon balance for the plume suggests that only 6% of the source term has been degraded in 50 years. The residual contaminant mass in the plume significantly exceeds estimates of electron acceptor inputs, indicating that the plume will grow. Two detailed vertical profiles through the plume show that contaminant distributions are controlled more by source history than by biodegradation processes. Microbiological and mass balance studies show that biodegradation is greatest at the plume fringe where contaminant concentrations are diluted by transverse mixing. Active bacterial populations exist throughout the plume but biodegradation is inhibited in the plume core by high contaminant concentrations. Stable isotope studies show that SO_4-reduction is particularly sensitive to contaminant concentration. The aquifer is not oxidant-deficient but natural attenuation of the phenolic compounds in this system is limited by toxicity from the pollutant load and the bioavailability of electron acceptors. Natural attenuation of these contaminants will increase only after increased dilution of the plume.

1.   Introduction

There is increasing interest in natural attenuation as a remedial option in the risk-based management of groundwater resources. The application of this technology requires that there is a framework in place for the robust assessment of its performance at individual sites. This framework needs to incorporate appropriate strategies for monitoring natural attenuation processes *in situ* and predicting the potential for natural attenuation at field scale.

Several technical protocols are available which provide a basis for the performance assessment of monitored natural attenuation schemes (Buscheck and O'Reilly, 1995; OSWER, 1997). These have evolved from experience of contaminated sites in North America, and are principally derived from studies of petroleum hydrocarbons and chlorinated solvents.

An important distinction is that there is little provision within these protocols for interpretation of natural attenuation within the hydrogeological settings and range of contaminated sites found in the UK and elsewhere in Europe. The UK has a legacy of contaminated industrial sites located on deep, consolidated, dual-porosity aquifers. Groundwater pollution from these sites often results in the development of complex plumes.

Coal-gasification plants are an important source of soil and groundwater pollution in the UK. Pollutant streams from these facilities typically contain a wide variety of organic and inorganic compounds (e.g. phenolic compounds and NH_4), usually at very high concentration. These phenolic compounds are normally biodegradable under a range of redox conditions (Suflita *et al.,* 1989; Klecka *et al.,* 1990; Rudolphi *et al.*, 1991). However, in comparison with other groups of organic pollutants, our understanding of the fate of pollutants from coal-gasification plants in UK aquifers is poor.

The objective of this paper is to present a combination of theoretical and field based methodologies which have been developed to assess the natural attenuation of a complex plume of phenolic contaminants in an important UK aquifer. A case study is used to describe a qualitative and quantitative framework for interpreting *in situ* biodegradation processes and evaluating the performance of natural attenuation technology at the site. The work forms part of a wider programme of research that seeks to develop methods to predict the potential for natural attenuation of organic pollutants in UK aquifers.

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2.   Case Study Investigation

2.1 Site Description and Investigation History

The plant was constructed in 1950 and since then has manufactured a range of organic chemicals, originally from coal-tar, but more recently from feedstocks brought in from elsewhere. The site overlies the Permo-Triassic Sherwood Sandstone, the second most important aquifer in the UK. Locally, it is a fluviatile red-bed sandstone with a porosity of about 26% and bulk hydraulic conductivity of about 0.7m d^{-1} (Aspinwall & Co., 1992). Groundwater levels are shallow (typically <5mbgl) and the aquifer is 250m thick in the vicinity of the site. Groundwater flow is westerly at 4-11m y^{-1}. The only receptor at risk is a public supply borehole, located approximately 2km west of the plant and >100 y travel time from the present plume.

The aquifer sediments contain abundant Fe and Mn oxides as grain coatings, minor particulate organic carbon and are calcareous at depth (below 50m). Background groundwater is aerobic and contains NO_3 and SO_4 at concentrations up to 33mg l^{-1} and 93mg l^{-1}, respectively.

A plume of phenolic compounds (phenol, cresols and xylenols) was discovered under the site in 1987. The initial site investigation used 22 boreholes, typically nested in groups of three, terminating at different depths and completed with 10m screens. The plume developed using data from these boreholes extends 500m westward and to a depth of 50m, when defined by the 10mg l^{-1} phenol contour. The current volume of the plume is about 3 million m^3. The total concentration of organic compounds in the source area is presently 24,800 mg l^{-1}, including 12,500 mg l^{-1} phenol. Site history and groundwater flow patterns suggest that spillages started soon after construction of the plant, that is, the plume is 50 years old. These spillages include mixtures of organic compounds and mineral acids, the latter giving rise to a SO_4 plume with concentrations up to 449mg l^{-1}. There is no information to indicate when spillages stopped, although the plume remains anchored by a strong source.

2.2 Groundwater Quality

The distribution of phenol and other selected groundwater quality data collected from the long screen boreholes is shown in Figure 1. Organic contaminant concentrations (represented by phenol) decrease along the plume flow path and at the plume fringe, relative to the core. These trends are reflected in the consumption of aqueous and mineral oxidants in the plume and corresponding increase in the concentrations of reduced inorganic species (NO_2, Mn^{2+}, Fe^{2+}, S^{2-}) and gases (methane), relative to the background groundwater. The plume also contains elevated concentrations of total inorganic carbon (TIC), relative to background groundwater (Figure 2). This data is clear evidence of *in situ* bioremediation of the organic compounds within the plume, at contaminant concentrations up to 12,500 mg l^{-1}, and
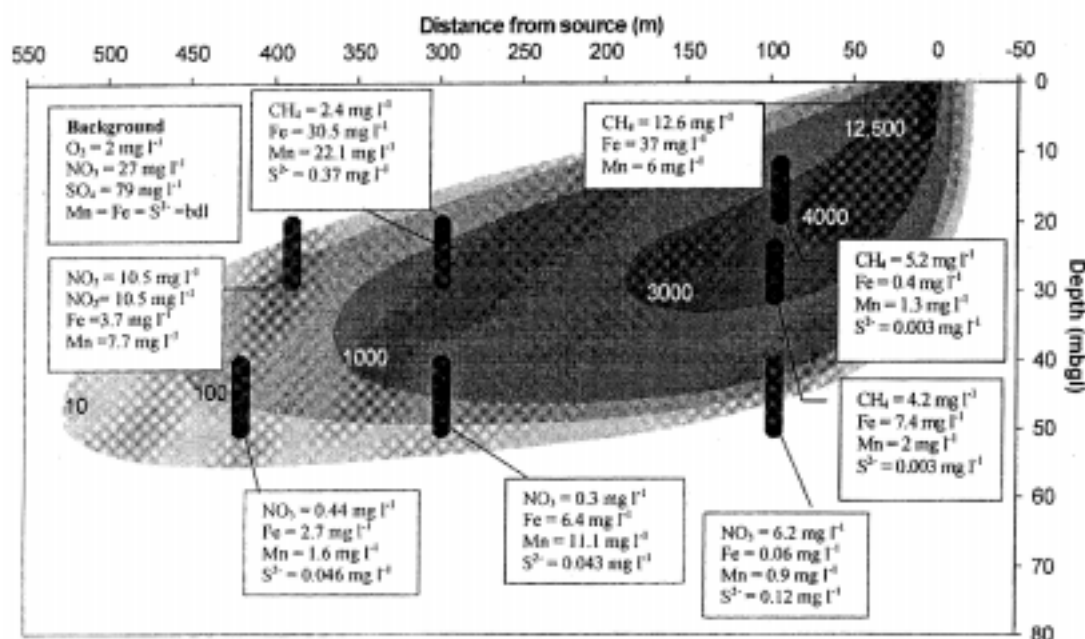

Figure 1.   Schematic cross section of phenol plume (mg.l^{-1}) beneath site with selected groundwater quality data. Borehole positions and screen length are shown in black.
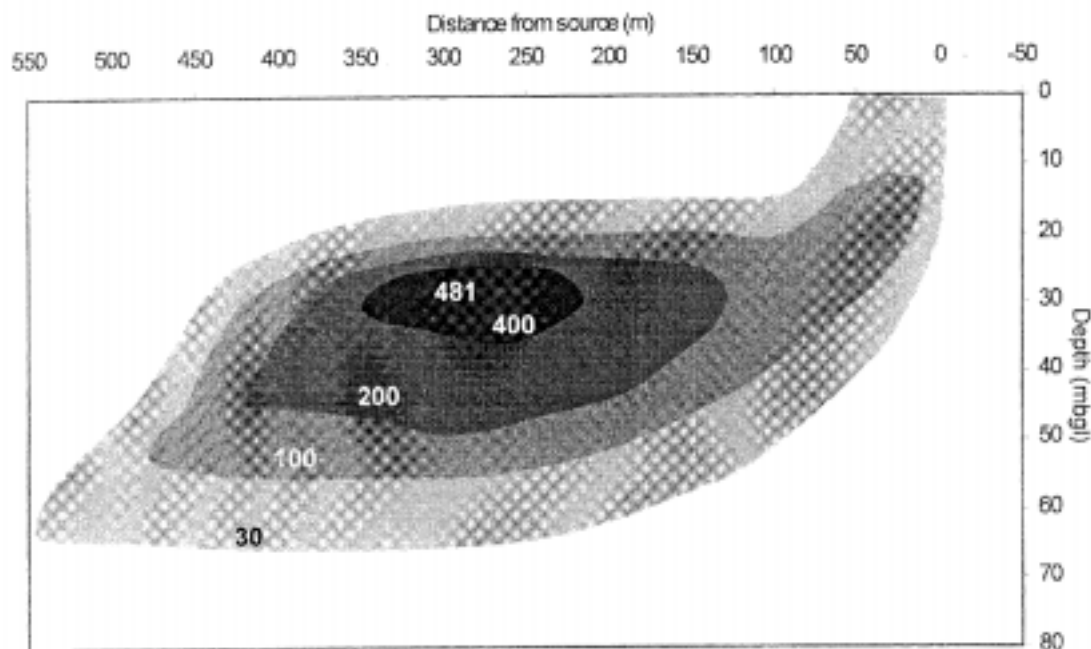
Figure 2.   Distribution of total inorganic carbon (mg.l^{-1}) in contaminated groundwater.

provides a good indicator of the likely range of redox processes involved (Borden *et al.,* 1995). The range of oxidative processes established from this information is summarized in Table 1, using phenol as the model compound.

2.3 Mass balance for the plume

A global mass balance can be constructed for the plume using the biodegradation processes and reactant concentrations identified from the groundwater surveys (Figure 1 and 2). The analysis can be completed in terms of an electron balance and carbon budget for the plume, using inputs of electron donors, electron acceptors and inorganic metabolites derived from the plume source, background groundwater and plume residuals. These inputs are formally linked by the reactions presented in Table 1 in a box model for the plume, which can be extended to include other organic contaminants (e.g. cresols and xylenols) and metabolites (e.g. methane). The conceptual framework underpinning this analysis is presented in Thornton *et al.* (1998).

An electron and carbon budget for the plume derived by using groundwater quality data collected from the long screen monitoring boreholes is displayed in Table 2. The residual electron donor fraction (contaminant-C) in the plume (6.8 x 10^8 e-) exceeds the estimated input of electron acceptors (0.24 x 10^8 e-). However, the total production of inorganic metabolites, as total inorganic carbon (TIC), in the plume is very similar to the total estimated quantity of electron acceptors consumed over the history of the site (difference of 0.18 x 10^8 e-). Geochemical modelling of the groundwater quality data indicates that there is no source or sink for TIC in the plume, suggesting that the TIC is conserved within the system. The results suggest that the electron balance is good and that the total amount of TIC produced provides an independent

Table 1.   Summary of Oxidation Processes for Phenol

Aerobic oxidation	$C_6H_6O + 7O_2 \rightarrow\rightarrow 6CO_2 + 3H_2O$
Reduction of nitrate	$C_6H_6O + 14NO_3 \rightarrow\rightarrow 6CO_2 + 14NO_2^- + 3H_2O$
Denitrification	$C_6H_6O + \dfrac{28}{5} NO_3^- + \dfrac{28}{5} H^+ \rightarrow\rightarrow 6CO_2 + \dfrac{14}{5} N_2 + \dfrac{29}{5} H_2O$
Reduction of sulphate	$C_6H_6O + \dfrac{7}{2} SO_4^{2-} \rightarrow\rightarrow 6CO_2 + \dfrac{7}{2} S^{2-} + 3H_2O$
Reduction of solid phase Mn oxide	$C_6H_6O + 14MnO_2 + 28H^+ \rightarrow\rightarrow 6CO_2 + 14Mn^{2+} + 17H_2O$
Reduction of solid phase Fe oxide	$C_6H_6O + 28FeOOH + 56H^+ \rightarrow\rightarrow 6CO_2 + 28Fe^{2+} + 45H_2O$

Table 2. Electron Balance for the Plume (10^8 e-)

Species	Input	Residual	Consumed	Created
Organic C		6.8		
O_2	0.017		0.017	
NO	0.152		0.152	
SO_4	0.132	0.063	0.069	
Mn(IV)			0.0015	
Fe(III)	(large)	(large)	0.00087	
Total EAs			**0.24**	
TIC		0.41		0.41
CH_4		0.0048		0.0048
Total C produced				**0.42**

Notes: EA: electron acceptor; TIC: total inorganic carbon

check on the amount of organic pollutants degraded, including an upper limit on the source term. The latter, comprising the residual organic compounds and TIC, is equivalent to 1816 tonnes of contaminant carbon. The TIC in the plume corresponds to degradation of only 6% of this estimated source term, providing a plume-averaged half-life of more than 250 years. Aqueous electron acceptor inputs appear to be of greater importance in contaminant degradation in the plume than mineral oxidants (Table 2). The latter provide a negligible contribution in the overall plume budget, although core analysis indicates that the reservoir of available Mn and Fe oxides is very large, and not depleted in the plume. Importantly, the mass balance indicates that the residual electron donor fraction in the plume is significantly greater than the electron acceptor input. This indicates that the supply or bioavailability of electron acceptors in the plume is insufficient to meet the demand arising from the current pollutant load and that the plume is likely to grow.

The electron donor source term remains uncertain, since assumptions had to be made as to the source strength and area for the mass flux calculations. In addition the balance is sensitive to electron acceptor inputs from transverse dispersion across the plume fringe. Work is presently underway to quantitatively evaluate the uncertainty in the input parameters for the plume box model, in order to constrain the mass balance and to assess the robustness of the methodology for application at other sites.

The electron balance is useful in understanding the role of different biodegradation processes in contaminant turnover and the status of a plume, but the model and data available cannot identify the environmental controls, which may be limiting biodegradation. In addition, the data collected from the long screen monitoring boreholes provides only a limited insight of the distribution of contaminants and biodegradation in the plume.

2.4 Vertical Profiles

Two high-resolution multilevel samplers (MLS) with monitoring points at 1m intervals, have been installed at 130m and 350m from the site, to depths of 30m and 45m, respectively, to provide detailed vertical profiles through the plume. Comprehensive surveys of the vertical distribution of hydrochemical parameters, microbiological determinands and stable isotope signatures of inorganic C and S species in groundwater from these installations have been completed. The surveys provide improved resolution of the plume characteristics and pollutant fate by sampling groundwater through uncontaminated and contaminated sections of the aquifer.

2.4.1 Contaminant Distributions

The distribution of contaminants in groundwater 350m from the site is shown in Figure 3. Four contaminant waste streams can be identified in the plume and contaminants are present over 20m depth but with marked spatial heterogeneity in their distribution.

Greater organic contaminant mass is present at lower depth in the profile. This distribution reflects the presence of two plumes, with a less concentrated plume at shallow depth. Concentrations of SO_4 are higher in the plume relative to background groundwater at this location, with peak values of 600mg l^{-1} at shallow depth. This reflects mineral acid spillages at the plant. Contamination from road salting activities and spillages of NaOH can be identified by higher Na concentrations in the MLS profile. The alkali spillages form a separate but overlapping plume at shallow depth (20-28mbgl). These contaminants have a similar vertical distribution in groundwater 130m from the site, although the concentrations of the phenolic compounds and SO_4 are much lower.
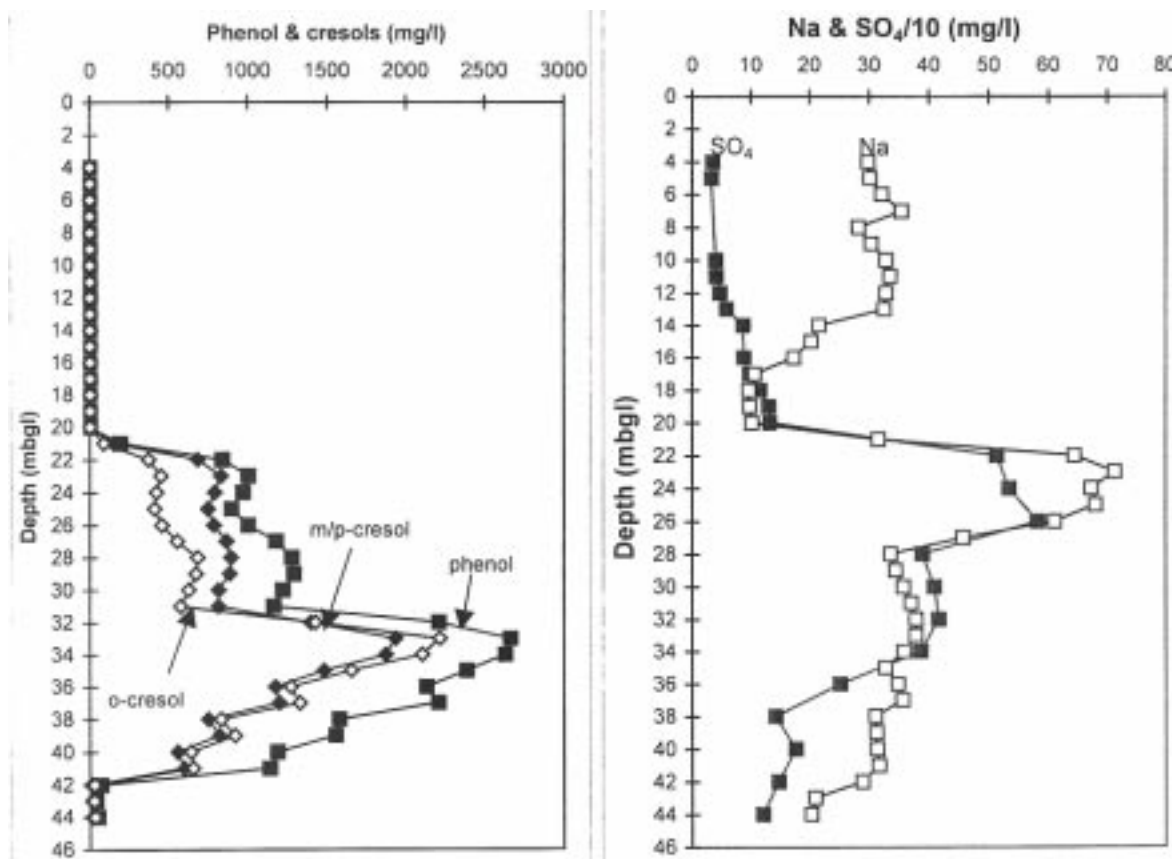
Figure 3.   Contaminant distribution in groundwater 350m from site.

The vertical profiles indicate that there have been episodic releases of organic and inorganic contaminants within the plume source area, with an earlier spillage of contaminants at much higher concentrations than that occurring later. There appears to have been little preferential attenuation of organic pollutants during transport.

2.4.2.   Range and Distribution of Redox Processes

The distribution of dissolved NO_3, Mn^{2+}, Fe^{2+} and S^{2-} in groundwater 350m from the site is shown in Figure 4. These profiles show that degradation of the phenolic contaminants is occurring under NO_3-reducing, Mn/Fe-reducing and SO_4-reducing conditions at different locations in the plume profile. Zones of methanogenesis have been detected at other locations in the plume.

Degradation under aerobic and NO_3-reducing conditions is restricted to the plume fringe, where sharp gradients occur in the oxidant profiles across a 1-2m mixing zone. Degradation under Mn/Fe-reducing and SO_4-reducing conditions appears to occur simultaneously across the plume profile. The S^{2-} profile indicates that SO_4-reduction is greatest at the plume fringe at this location, or that there is greater removal of reduced S in the plume core, via precipitation of Fe sulphide phases.

2.4.3.   Aquifer Degradation Potential

A conceptual model of aquifer degradation potential for these phenolic compounds can be developed from the groundwater chemistry, microbial ecology and biodegradation processes identified in the plume from the vertical profiles. Elevated concentrations of TIC (Figure 2) and organic metabolites (4-hydroxybenzaldehyde and 4-hydroxybenzoic acid) in the plume confirm contaminant mass loss due to degradation of the phenolic compounds (Figure 5). These species are also present above background levels in groundwater sampled in the vertical profile at 130m from the site.

The presence of organic metabolites in the vertical profiles indicates that degradation is occurring under all redox conditions found in the plume. However, the extent of contaminant degradation is strongly influenced by contaminant concentration and oxidant availability. A carbon mass balance for the vertical profiles and stable isotope studies shows
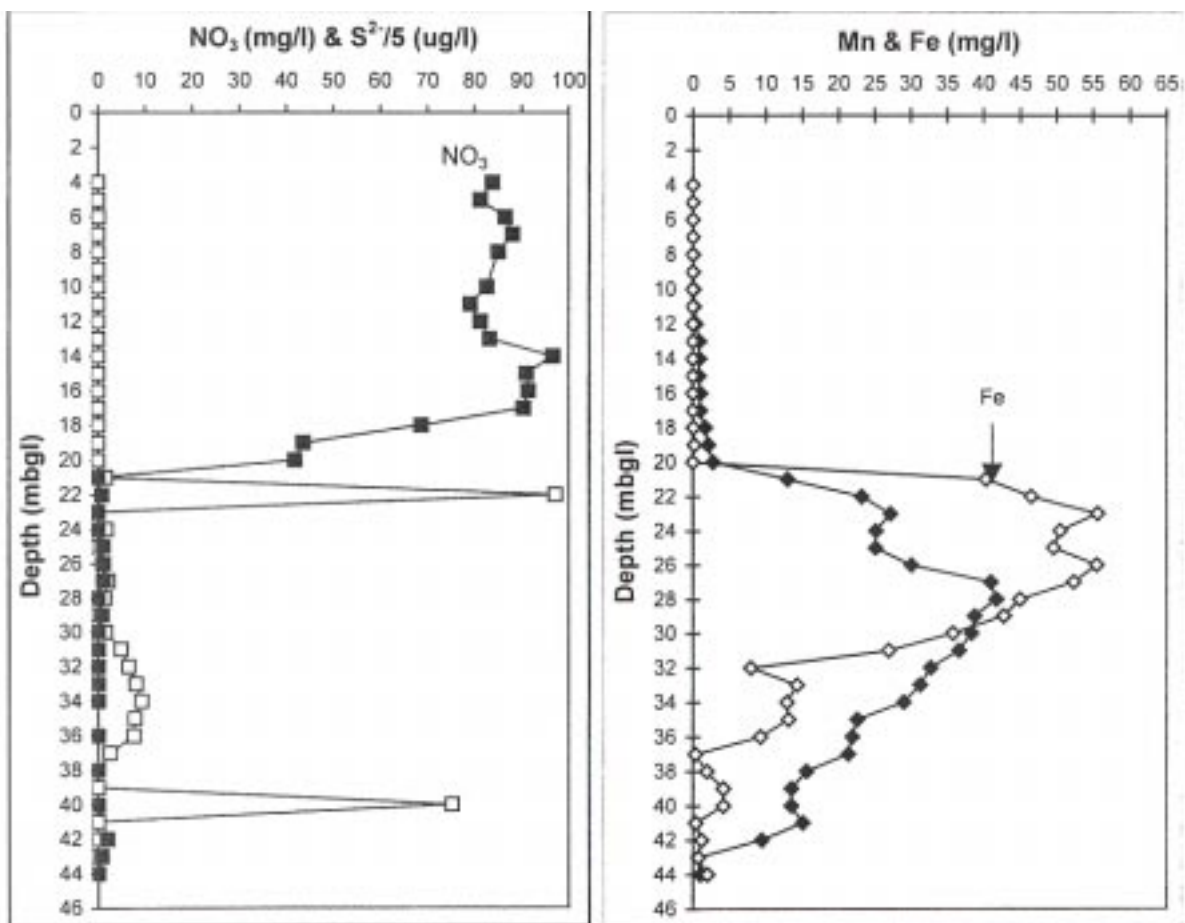
Figure 4.   Redox–sensitive species in groundwater 350m from site.

that SO_4-reduction and production of TIC from degradation is highest in zones of lower contaminant concentration (<1800mg I^{-1} total phenolics) at shallow depth within the plume. Degradation under Mn and Fe-reducing conditions occurs throughout the plume but is less sensitive to contaminant concentration than SO_4- reduction. However, the mass balance for the profiles confirms that the consumption of mineral oxidants (Fe^{2+}, Mn^{2+}) is negligible, despite their abundance on the aquifer sediments. This analysis also shows that dispersion of oxidants into the plume accounts for most contaminant mass degraded, with NO_3 being the most important oxidant consumed. These trends suggest that the potential for degradation is higher at the plume fringe where contaminant concentrations are diluted by transverse mixing.

However, the aerobic fringe is very narrow, despite the age and travel distance of the plume. Low dispersion restricts dilution and slows the input of energetically favourable O_2 and NO_3 oxidants. Hence, despite the presence throughout the plume of microbial populations capable of utilising these oxidants, these degradation processes are limited by electron acceptor supply at the plume fringe. Contaminant turnover is lower in the plume core where contaminant concentrations are greater and probably inhibitory to degradation. This is supported by microbiological studies, which show that microbial diversity and activity is much higher at the plume fringe than in the plume core. Culturable bacteria can be measured at all levels in the plume, although cell counts become depressed as contaminant concentrations increase, indicating that microbial populations are stressed by the environmental conditions and/or organic pollutant loading found in the plume core. Microbiologically, the plume is virtually inactive at 350m from the site, where the highest contaminant concentrations have been found.

2.5.   Performance Assessment of Natural Attenuation

A qualitative assessment of the performance of natural attenuation for this system can be made using the information obtained from the different investigative methodologies employed. This assessment is summarized in Table 3.

The analysis presented in Table 3 indicates that both *in situ* degradation and contaminant mass loss can be demonstrated in groundwater at the site using conventional indicators. However, these processes are severely limited
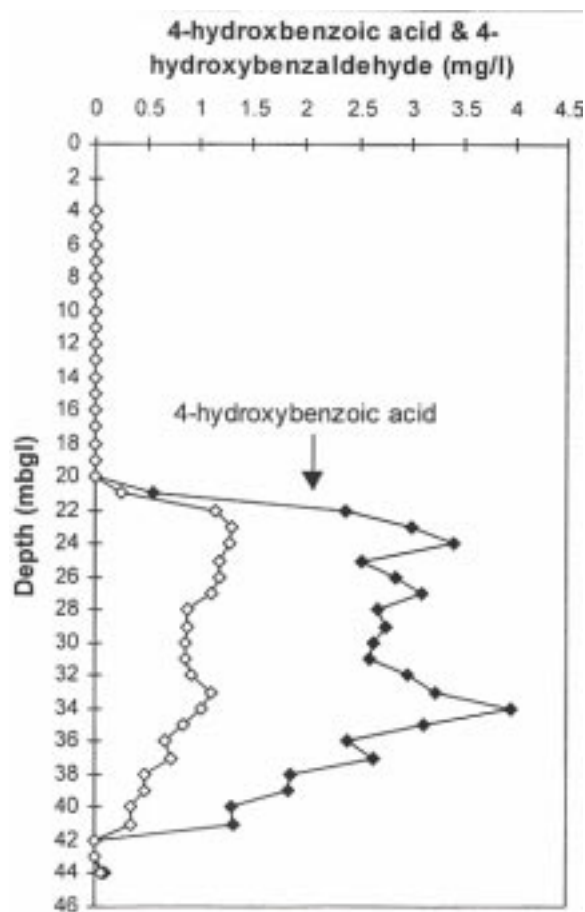
Figure 5. Organic metabolites in groundwater 350m from the site.

Table 3. Performance Assessment for Natural Attenuation at Site

Indicator	Phenolic plume	Comment
Mass reduction	Yes	Only 6% in 50 years
Products	Organic metabolites, TIC & methane	
Reduced electron acceptors	No O_2, NO_3 but Mn, Fe, S in solution	Incomplete Fe or SO_4- reduction
Microbial activity & diversity	High at plume fringe but low in core	Always measurable
Conclusion	NA insufficient	Constrained by: 1. Electron acceptor inputs 2. Toxic concentrations

by the environmental conditions in the plume and are occurring at rates which are too slow for natural attenuation to be effective. The primary factor limiting the natural attenuation of these organic pollutants appears to be the very high contaminant loading in the aquifer, which is inhibitory to degradation in much of the plume. Natural attenuation of the phenolic compounds is likely to increase only by increased dilution of the plume.

3.   Conclusions

   Approaches presently used to evaluate the performance of monitored natural attenuation schemes in contaminated aquifers may not adequately characterize the fate of pollutants in plumes with complex source histories. The combination of methodologies illustrated in the case study provides an improved basis for the performance assessment of natural attenuation in complex plumes. The results indicate that a range of biodegradation processes and mass loss can be demonstrated in contaminated groundwater at the site, in accordance with criteria found in current technical protocols for evaluating natural attenuation. However, although the phenolic compounds are biodegradable under the range of redox

conditions identified in groundwater and the aquifer is not oxidant limited, the plume is likely to grow. This is because contaminant concentrations remain toxic to degradation in much of the plume core and the supply of aqueous oxidants, via mixing with uncontaminated groundwater, is insufficient to meet the demand from the plume. Natural attenuation of these organic pollutants in this system is therefore likely to be ineffective under the present conditions and will only increase after increased dilution of the plume.

4.   Acknowledgements

5. References

Aspinwall & Co. (1992). Site Investigation at Synthetic Chemicals Limited, Four Ashes: Phase 6 Report

Borden, R. C., Gomez, C. A. and Becker, M. T. (1995). Geochemical indicators of intrinsic bioremediation. *Ground Water*, 33, 180-189.

Buscheck, T. and O' Reilly, K. (1995). Protocol for monitoring intrinsic bioremediation in groundwater. Chevron Research and Technology Company, pp. 20.

Klecka, G. M., Davis, J. W., Gray, D. R. and Madsen, S. S. (1990). Natural bioremediation of organic contaminants in ground water: Cliff-Dow Superfund site. *Ground Water*, 28, 534- 543.

OSWER (1997). Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites, Directive 9200.4-17, US EPA.

Rudolphi, A., Tschech, A. and Fuchs, G. (1991). Anaerobic degradation of cresols by denitrifying bacteria. *Archives of Microbiology*, 155, 238-248.

Suflita, J. M., Liang, L. and Saxena, A. (1989). The anaerobic biodegradation of o-, m- and p-cresol by sulfate-reducing bacterial enrichment cultures obtained from a shallow anoxic aquifer. *Journal of Industrial Microbiology*, 4, 255-266.

Thornton, S. F., Davison, R. M. Lerner, D. N. and. Banwart, S. A. (1998). Electron balances in field studies of intrinsic remediation. M. Herbert and K. Kovar (eds), *GQ 98—Groundwater Quality: Remediation and Protection*. Proceedings of a conference held at Tübingen, September 1998. IAHS publication 250: 273-282.

Soil Cleanup Policy and Monitored Natural Attenuation in the Netherlands
(Dr. Joop J. Vegter, The Netherlands)

Introduction

Natural attenuation, more specifically monitored natural attenuation, is advocated as a low-cost solution for soil remediation. It involves degradation of pollution by natural processes. Up till now the cleanup of contaminated land was based on civil engineering approaches aiming at maximum risk control (excavation or containment of polluted soil). From a technical point of view, these approaches are still the fastest way to solve the problem. In a crowded country like the Netherlands, there is a heavy pressure on re-utilization of polluted sites, so fast remediation is an advantage. However the high costs associated with these methods are also a big disadvantage and were prohibitive in many redevelopment projects. On the other hand, extensive cleanup methods like natural attenuation or in situ biodegradation are less costly but require more time, have less-predictable results and may require long-time monitoring and aftercare. This is a drawback if land can only be reused after the cleanup. A recent change in cleanup policy may provide the opportunity to have the best of both worlds: Fast cleaning of the upper layer of the soil, which does directly affect the possibilities to reuse the land, and slower cleaning of groundwater by extensive and less-costly methods like natural or enhanced natural biodegradation.

This new policy is still under construction but even when operational it may not provide very detailed generic regulations on natural attenuation. Whether natural attenuation is successful will depend on site-specific conditions. These are never completely known, and processes like biodegradation and chemical and physical behavior of contaminants may be difficult to predict. Cleanup by natural attenuation may better be considered as an experiment under controlled conditions. The authorities will have to provide some room for these experiments in terms of time and space. The control of these experiments will require monitoring of the process. At certain points in time one must be able to decide whether natural attenuation is performing as expected or whether one has to resort to other cleanup methods or to containment. Because groundwater pollution is mobile, it has to be treated as a source of soil contamination, which means that extensive cleanup solutions must be brought in line with policies concerning the prevention of soil and groundwater pollution.

Soil Protection Policy Framework

Prevention of soil pollution in the Netherlands is based on the Soil Protection Act, which came into force in 1987. In 1994, the Soil Cleanup Act was incorporated in the Soil Protection Act. Prevention of soil pollution and cleanup of polluted sites have the same legal base, permitting an integrated soil protection policy for the soil, including groundwater and sediments.

Central to the Dutch soil protection policy is the principle of soil multifunctionality. According to this principle, the number of functions that a soil can have should not be reduced by human activities, in order to keep all options open for actual and future landuse. (Moen et al. 1986, Moen 1988, Vegter et al. 1988). Soil has to be preserved and protected as a valuable resource for the future. The Dutch soil protection philosophy is in line with the European Soil Charter published by the Council of Europe (1972), and with ideas about sustainable development as set out by the Brundtland Committee of the UN (WCED, 1987). Because restoration of contaminated land is considered as a part of soil protection, the multifunctionality principle applies to soil cleanup as well. However, in view of the technical difficulties and financial problems caused by the large number of contaminated sites, this principle no longer applies for so called historical contamination (contamination resulting from activities dating from before 1987, the year of enforcement of the Soil Protection Act). Cleanup objectives for those situations will depend on the actual or intended use of the land. They will also involve groundwater cleanup by cost effective means (including bioremediation and natural biodegradation). This brings Dutch policy in line with other countries where soil protection and cleanup of contaminated land were less tightly linked (Visser, 1993).

General procedures for investigation and remediation of polluted sites are published in a guideline, the Soil protection guideline. It is a newer version of a guideline datingfrom 1983, which contained the well-known ABC-list of trigger-values. The ABC-values were not intended to be used as generic soil quality standards (Moen et al., 1986). Information about the geohydrological conditions at the site, which control transport and diffusion of pollution to surrounding areas, and the use of the soil which determines exposure and the risks involved had to be considered as well. Due to the more-difficult qualitative nature of the latter criteria, the ABC-values became the main tools for decision making, and were adopted by

many countries as a starting point for the assessment of soil contamination (Visser, 1993). In view of the limitations of the former ABC-system, a new system was introduced in 1994, with two sets of generic criteria: Target values and Intervention values. In addition, more guidance on site specific assessment is provided, together with criteria to assess the urgency of a remediation.

Soil And Groundwater Remediation

Decisions about cleanup of soil contamination involve a number of stages and are based on generic quality criteria for soil and groundwater and site specific considerations.

The scientific rationale of the generic criteria, the Target values and the Intervention values, is described by Robberse & Denneman (1993) and Vegter (1993). They are used in the first stages of the assessment. Site specific assessment is made in later stages. During an assessment the following questions must be answered:

- Is the site seriously polluted?

- Is remediation urgent?

- What is the remediation objective for the site?

Serious Pollution?

Suspect sites are first subject to a preliminary investigation. The history of the site is studied in order to yield indications about the nature of the polluting substances. Soil and groundwater are sampled. Concentrations of pollutants are compared with two sets of soil quality criteria: Target values (former A-values) and Intervention values (former C-values). If contamination of soil and/or groundwater exceeds the average of the Target value and the Intervention value, a further and more extensive investigation must be carried out.

If the results of a further investigation indicate contaminant levels above the Intervention value the site is registered. The official terminology for a site where Intervention values are exceeded is "serious pollution". Registration means that authorities are entitled to perform a cleanup based on the Soil Protection Act. Cleanup of less-polluted sites, which might be considered necessary for other reasons, cannot be part of the soil cleanup program based on the Soil Protection Act and cannot be financed by this program.

Is Remediation Urgent?

The urgency for cleanup is dependent upon the actual human exposure, the ecological impact and the mobility of the pollution. Human exposure is assessed by using a computer model, called CSOIL (Berg, R van den, 1995). In view of the uncertainties of this model, additional measurements of contact media such as indoor air and characteristics of contaminants in homegrown vegetables is necessary in most cases. If exposure exceeds Tolerable Daily Intake (TDI)[1] or Maximum Tolerable Risk (MTR) remediation is urgent. Ecological impact is dependent on the (eco)toxicity of the pollutant, the size of the polluted area and the use of this area. The soil protection guideline states that there is an actual ecological risk unless:

The extent of the pollution exceeding HC50 is less than:

- 50 m^2 for nature areas

- 5000 m^2 for residential and agricultural areas

- 0.5 km^2 for cities and industrial areas.

The extent of the pollution exceeding 10*HC50 is less than:

- 50 m^2 for nature areas

- 50 m^2 for residential and agricultural areas

- 5000 m^2 for cities and industrial areas.

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[1]The TDI is comparable with the Acceptable Daily Intake (ADI)for contaminants which is recommended by the WHO

Groundwater pollution is of major concern in the Netherlands. Remediation is considered urgent if the following conditions apply:

• There is a NAPL (Non-Aqueous Phase Liquid) layer

• There is dispersion into surface water or transport of polluted sediments

And

• The increase in the amount of polluted soil exceeding intervention values is larger than 100 m3 per year

• Transport by groundwater is detectable

A timetable for remediation of urgent sites will be made in each province or larger city by the provincial or municipal authorities. The most urgent sites have to be remediated within 4 years. A full description of the procedure for determining the date that an urgent remediation has to start is beyond the scope of this paper. A more extensive overview of Dutch cleanup policies is given by Denneman (Denneman, 1999). Nonurgent sites will remain registered, but are not included in the timetable. Urgency of these sites is reassessed if land use or the geohydrological situation changes.

What is the objective of the remediation?

Decisions about the objectives of a cleanup depend on the history of a site. If the site was polluted after 1987, the year the Soil Protection Act came into force, a complete cleanup of all pollution is mandatory. Pollution dating from before 1987 is seen as a legacy from the past, when people were not fully aware of the need to protect the soil environment. The cleanup policy for these situations has changed recently and to put this policy into practice, a land-use related policy (functional cleanup) is now being developed. The former policy did emphasize the restoration of soil multifunctionality (all options for future use had to be restored) as the preferred cleanup goal. Other solutions were allowed if technical, financial or environmental problems prohibited a complete cleanup. This policy led to difficulties when put into practice especially in urban redevelopment where the actual risk of the pollution is rather low, but where the soil is unfit for it's intended use. Soil cleanup is now considered from both an environmental policy and a spatial planning policy point of view, and a so-called functional approach provides a tighter linkage between cleanup goals and intended use of the land.

The new approach does not merely consist of the derivation of some risk-based land-use dependent target values, but considers the design of sustainable land-use specific solutions as a starting point. The design is based on a conceptual model, which makes a distinction between the upper layer of the soil, a so-called contact zone, where the quality of the soil determines the possibilities to use the land, and deeper layers where contaminants are only of concern as far as they affect groundwater and other areas due to dispersion. Because immobile pollutants which do not disperse in groundwater can remain in the soil as long as the contact layer meets it's requirements for land-use, this type of solution can be very cost-effective. Furthermore intensive cleanup techniques, like excavation and ex situ cleaning, which are more expensive than extensive techniques, may be needed for the upper layer of the soil only. The conceptual model is illustrated in figure 1.

In the new approach, a cleanup solution based on the conceptual model will have to meet the following general policy objectives:

• Cleanup solutions should be based on an integrated approach of soil and groundwater contamination

• The soil should meet the requirements of its use (fitness for use) by:
   - Reducing exposure of human beings and use related ecological endpoints
   - Preventing dispersion of pollution in groundwater

• The cleanup procedure must be monitored and allow for corrections and changes in the approach if necessary.

• The cleanup should minimize aftercare

The minimal requirements of the contact zone in relation to landuse and the minimal requirements for groundwater cleanup including natural attenuation are presently discussed. For the contact zone, two types of requirements are needed. One concerns the thickness of the contactzone (usually between 0.5 and 1.5 meter) and the other is quality of the soil in that layer expressed as concentrations of the relevant contaminating substances. Because the contact zone can be considered as a construction that can be standardized, generic quality criteria can be used, which is a big advantage for the implementation of the new approach. However, in some cases adjustments may be needed, so custom made solutions for contaminated land are also allowed as long as the general policy objectives are met.
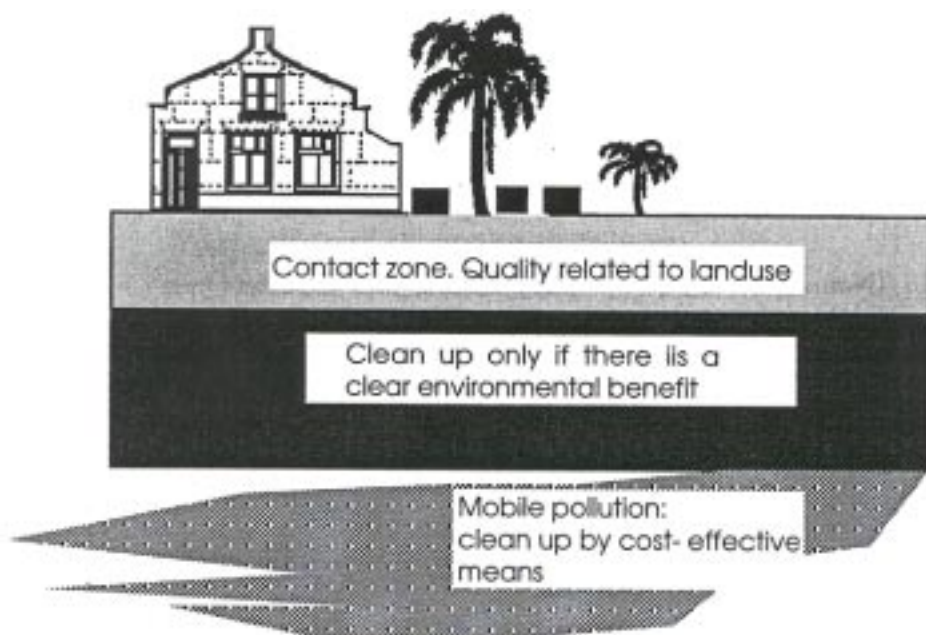
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Figure 1. Conceptual model for cost effective cleanup solutions.

Numerical criteria for permissible contaminant levels in contact zones will be based on the following considerations, of course in relation to landuse:

• Human health

• Plant growth, (domestic) animals

• Soil processes (soil microbiology)

• Quality of food products

Implicit in the approach is that the pollutants that may remain in the contact zone are not mobile so that groundwater is not affected. Further numerical details on quality objectives and the number of different types of landuse are presently discussed.

For groundwater cleaning, the goal is cleanup by cost effective means within a time frame of 30 years. Furthermore, the cleanup goal has to be reached by (bio)degradation of the pollutant and not merely by dilution. So, the occurrence of biodegradation must be plausible from a scientific point of view and must be shown to occur during the time allowed for the cleanup. This will require sound monitoring strategies. It will also be very important to address the problem of residual contamination in the light of the EU groundwater directive, which prohibits discharges of hazardous substances in groundwater. During a cleanup based on monitored natural attenuation some dilution and dispersion of pollution will always occur. Natural attenuation may also be enhanced by addition of substances to soil and groundwater in order to stimulate microbial activity. If the presence of these substances and residual contamination is temporal or has negligible effects on the quality of the groundwater, this may be considered acceptable from a soil and groundwater protection point of view. It is up to the policymakers to find the right balance between soil cleanup and soil protection in these cases.

References

Berg, R van den (1995): (CSOIL, report in Dutch) Blootstelling van de mens aan bodemverontreiniging; een kwalitatieve en kwantitatieve analyse, leidend tot voorstellen voor humaan toxicologische C-toetsingswaarden, herziene versie, RIVM, Bilthoven, The Netherlands Report no. 725201006

Council of Europe. European Soil Charter, Ref: B(72) 63, Strasbourg 1972.

Denneman, C.A.J., 1999. In : Risk assessment for contaminated sites in Europe. Volume 2: Policy Frameworks. CARACAS (Concerted Action on Risk Assessment for Contaminated Sites in the European Union), C. Ferguson & H. Kasamas eds. ISBN 0 953 3090 1 0.

Moen, J.E.T., 1988. Soil protection in the Netherlands. In: Contaminated Soil '88. Second Int. TNO/BMFT Conference on Contaminated Soil. K. Wolf, W.J. van den Brink, F.J. Colon (eds). Kluwer Academic Publishers.

Moen, J.E.T., J.P. Cornet & C.W.A. Evers, 1986. Soil protection and remedial actions: criteria for decision making and standardization of requirements. In: Contaminated Soil, First Int. TNO Conference on Contaminated Soil. J.W. Assink & W.J. van den Brink (eds). Martinus Nijhoff Publishers.

Robberse, J.G. and C.A.J. Denneman, 1993. Do target values help to protect the soil. In: Contaminated Soil '93, 373-382. Fourth Int. KfK/TNO Conference on Contaminated Soil. F. Arendt, G.J. Annokk_e, R. Bosman & W.J. van den Brink (eds). Kluwer Academic Publishers.

Vegter, J.J., J.M. Roels & H.F. Bavinck, 1988. Soil quality standards: Science or science fiction - an inquiry into the methodological aspects of soil quality criteria. In: Contaminated Soil '88. Second Int. TNO/BMFT Conference on Contaminated Soil. K. Wolf, W.J. van den Brink, F.J. Colon (eds). Kluwer Academic Publishers.

Vegter, J.J., 1993. Development of soil and groundwater cleanup standards in the Netherlands. In: Developing cleanup standards for contaminated soil sediment & groundwater, How clean is clean? Specialty conference proceedings, Water Environment Federation TT042, 1993.

Visser, W.J.F., 1993. Contaminated land policies in some industrialized countries. TCB R02 (1993), The Hague

World Commission on Environment and Development, 1987. Our common future. Oxford University Press, Oxford.

Experiences with Obtaining Regulatory Approval for Natural Attenuation at a Closed German Refinery (Terry Walden[1] and Michael Paersch[2])

Abstract

In 1985 BP closed its 80-hectare refinery in Hunxe, Germany in the North Rhine-Westphalia state in the western central region of the country. Over the next ten years extensive remediation was conducted, including on-site bioremediation of over 26,000 tons of soil, pump-and-treat, and use of dual phase extraction for free product recovery. A total of 260 tons of product were removed from the soil and groundwater.

Over time however, it became clear that a total cleanup of the saturated zone was neither technically achievable nor economically practical. Three separate TPH (total petroleum hydrocarbons) and BTEX plumes existed, but a numerical groundwater modeling study showed the plumes to be stable within the boundaries of the BP property. Furthermore a risk assessment indicated no threat to future land users if groundwater abstraction were restricted in the contaminated region. On this basis BP negotiated an agreement with the regulators to terminate the remediation while selling the land for industrial development. It is believed this is one of the first instances of explicit demonstration of risk assessment and monitored natural attenuation in Germany.

The terms of the public sector contract regarding the land sale are that a monitoring program has been put in place for an indefinite period to verify that natural attenuation is occurring and the modeling forecasts remain accurate. Ground-water utilization is restricted to irrigation use only. BP retains liability under the *polluter pays* principle and would be required to re-implement an active remediation program if conditions change and a risk to human health or the environment is later identified.

1. Introduction

From 1960 to 1985 BP Germany operated its Ruhr Refinery near the city of Duisburg, Germany in the district of Wesel. The site occupied a total area of 153 hectares on relatively flat land. Operations ceased in 1985 and part of the site was converted to a terminal. However the former refining area, which occupied an area of 80 hectares, was demolished, the land was cleared and a remediation program put in place with a view towards selling this part of the site for re-development.

The site, shown in Figure 1, is bordered to the north by a canal, which is located about 300 m south of the region's main watercourse, the River Lippe. To the east and south-east, the site borders a series of public water drinking wells, but these are hydraulically upgradient. A forest and meadow nature reserve is located to the south, and a residential area of houses with small gardens lies to the west.

The soil consists of man-made fill in the upper 1.3 m with loamy sands up to 3 m thickness below the fill. Medium sands to gravel underlie the loam up to a thickness of 22 m. Groundwater is encountered in the medium sands within an unconfined aquifer approximately 6 m below ground surface. The groundwater flow direction is towards the north/north-west in the direction of the canal. With the relatively permeable sands (conductivity of 1.5×10^{-1} cm/s), the calculated flow velocity is as high as 0.55 m/day.

2. Remediation Program

The entire refinery and terminal site was investigated in 1987/88 to determine the nature and extent of contamination. These included the installation of 180 monitoring wells and 1200 soil borings with the analysis of approximately 4000 soil and groundwater samples. Most of the investigation activities were concentrated in the former refining process area.

Between 1988 and 1995 a number of remediation systems were implemented. A total of 27 pump-and-treat recovery wells were installed to recover free product and treat dissolved phase TPH and BTEX contamination. Over the 80-hectare process area, the Umweltschutz Nord process (consisting of periodically turned compost piles in enclosed tents)

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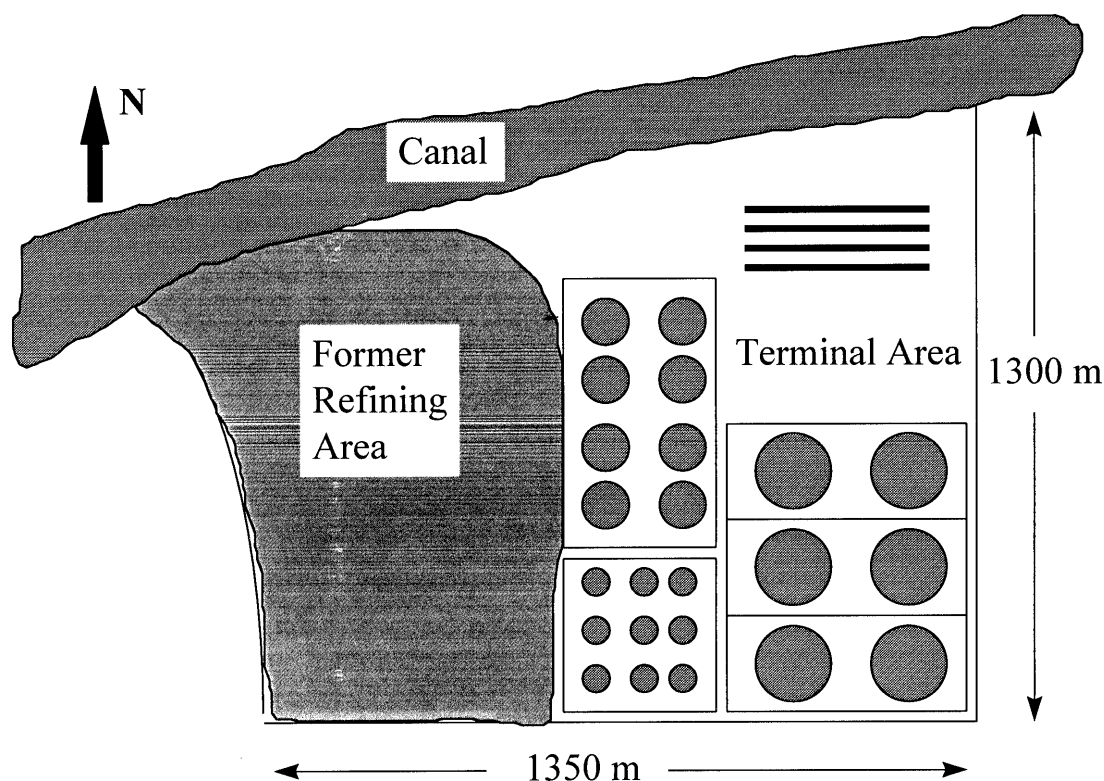
Figure 1. Site layout including former process area sold for re-development.

was conducted to bio-treat the unsaturated zone soil to an agreed target of 800 mg/kg TPH, after which the soil was re-deposited in the ground.

Although the unsaturated zone was cleaned, the capillary fringe and smear zone remained contaminated with free and dissolved phase BTEX/TPH. Recovery wells were installed to reduce the thickness of free product, and a series of soil vapor extraction, hydrogen peroxide injection, in-situ air sparging and dual phase extraction pilot tests were conducted from 1992 to 1994 to address the residual phase. Air sparging showed the most promise but small heterogeneities in the saturated soil profile prevented effective distribution of air into the smear zone. By 1994, the amount of free phase was reduced considerably (thickness of free phase less than 10 cm), while dissolved phase BTEX/TPH concentrations varied from 10 to 35 mg/l.

3.   Natural Attenuation

By year end 1994 it was becoming increasingly obvious that active groundwater treatment would not achieve drinking water standards in any reasonable time frame. Further the concept of risk assessment and natural attenuation began to emerge in Europe following its introduction in the United States. Discussions began with the local regulators on applying these strategies to the former refining area under an industrial re-development scenario.

Three plumes exist in the former refining area. Figure 2 shows the plumes, which are labeled as the Flare Field, Process Field and Aromatics Field.

The plumes were artificially truncated by groundwater remediation wells at this time, so a modeling study was conducted to ascertain the distance over which a stable plume length would be established when remediation was terminated. With the significant amount of well data available for the site, a numerical model (MT3D) was run for this purpose. For situations where the source is not removed, biodegradation is the sole process limiting plume growth. Concentration vs. Time and Distance data were used to calculate a first- order biodegradation rate for the principal aromatic fractions in each plume. For the Flare and Process fields where benzene was the major component, a half life of 120 days (decay rate of 0.006 per day) was used. For the Aromatics field which was composed almost entirely of xylene, a half life of 55 days (decay rate of 0.012 per day) was calculated. Figure 2 shows the modeling results. It shows that each of the plumes stabilize within the boundary of the site.
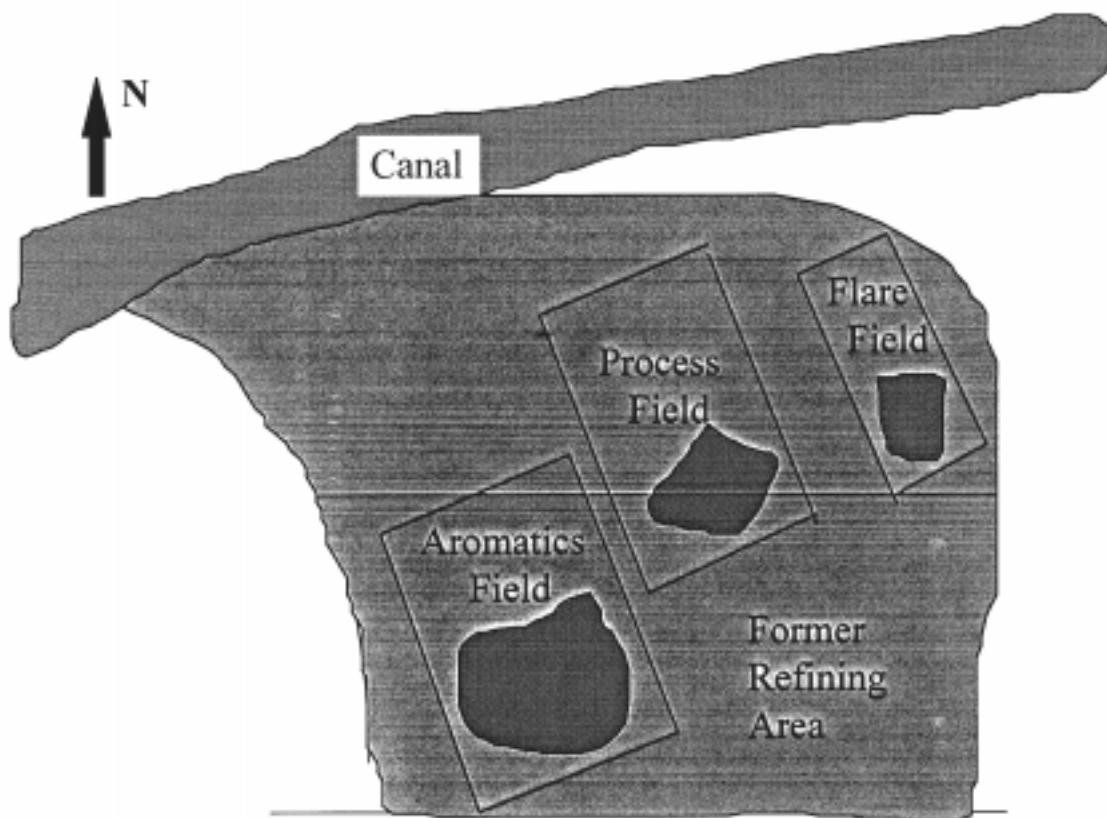
Figure 2.   Plumes and the modeled zones where they would stabilize

4.   Risk Assessment

Although significant concentrations of residual and dissolved phase hydrocarbon existed in both the smear zone soil and groundwater, a risk assessment was conducted utilizing the BP's internal RISC (Risk-Integrated Software for Clean-ups) program. The key findings from this exercise were the following:

- Groundwater plume concentrations and free phase thickness had reduced significantly since 1987

- Further reduction of groundwater concentrations in the source area is technically difficult due to soil contamination in the smear zone and water table fluctuations which periodically induce groundwater loading

- There is no offsite groundwater migration and therefore no threat to the public water drinking wells to the south-east or to the residential areas to the west.

- Groundwater impact onsite presented no unacceptable human or ecological risk. This includes vapor emissions into future buildings or direct contact through the irrigation pathway. Drinking water use onsite however must be restricted.

5.   Legal Agreement

The combination of the risk and plume stability arguments, the open and the trusting relationship between BP and local regulators, and BP's willingness to accept liability and take action if a subsequent threat to the public was identified, prompted an historic agreement between BP and the district of Wesel on September 6, 1996. This public sector contract between the two parties addressed how liabilities are to be regulated in private purchase contracts between BP and buyers of the land. The key terms of this contract are as follows:

- All remediation systems can be immediately terminated while allowing the sale and re- use of the land for industrial purposes to proceed

- A monitoring system is to be put into place to measure TPH and BTEX in 12 wells, starting at monthly intervals in the first half year, then progressing to quarterly, semi-annual and annual intervals in each succeeding year. No finite period for the monitoring program is specified

- Groundwater wells for drinking water are restricted and the authorities must approve the installation of a well and use of the water for any other purpose

- Excavation of the ground is limited to within 2 m of the groundwater table

- Under the *polluter pays* principle, BP (not the new owners) retains indefinite liability and will re-start active remediation if a danger to public safety is recognized

This agreement is the first known instance in Germany where natural attenuation was explicitly recognized as a remedy of choice. There are several cases where groundwater remediation was terminated when concentrations reached asymptotic values, even though the target value was not achieved. But the Hunxe site represents the first known German example where MNA (monitored natural attenuation) was implemented.

6.   Epilogue

To date, approximately 50% of the land has been sold to third parties. These are mostly small industrial companies, including a recycling contractor, a metal-working firm, a carpentry shop, etc. More of the land is expected to be re-developed in the coming year.

Although BP's liability with respect to the groundwater is unlimited in time under German legislation, in practice BP has put a 10-year limit into its private land purchase contracts. This is a practical solution to enable the company to *close the books* on the site while granting sufficient time to ascertain whether any future problems could arise.

The monitoring program to date has verified the predictions from the modeling study, at least in the Flare and Process fields. Discussions may likely take place with the authorities in the near future regarding termination of these activities. There has been less consistency in the Aromatics field with some fluctuations in concentrations and plume dimensions occurring. Monitoring of this plume will therefore continue for the foreseeable future.

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