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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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NATO/CCMS Pilot Study

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

Rome, Italy
May 5-10, 2002

January 2003

NOTICE

This Annual Report was prepared under the auspices of the North Atlantic Treaty Organization's Committee on the Challenges of Modern Society (NATO/CCMS) as a service to the technical community by the United States Environmental Protection Agency (U.S. EPA). The report was funded by U.S. EPA's Technology Innovation Office. The report was produced by Environmental Management Support, Inc., of Silver Spring, Maryland, under U.S. EPA contract 68-W-00-084. Mention of trade names or specific applications does not imply endorsement or acceptance by U.S. EPA.

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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 reports on the fourth 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 was successfully concluded in 1991, and the results were published in three volumes. The second phase, which expanded to include newly emerging technologies, was concluded in 1997; final reports documenting 52 completed projects and the participation of 14 countries were published in June 1998. Through these pilot studies, critical technical information was made available to participating countries and the world community.

The Phase III study, which concluded in 2002, focused on the technologies for treating contaminated land and groundwater. The study addressed issues of sustainability, environmental merit, and cost-effectiveness, with continued emphasis on emerging remediation technologies. The objectives of the study were 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 Phase III Mission Statement is provided at the end of this report.

The Phase III pilot study meetings were hosted by several countries and at each meeting, a special session was held for the discussion of a specific technical topic. The meeting dates and locations were:

- February 23-27, 1998: Vienna, Austria
- May 9-14, 1999: Angers, France
- June 26-30, 2000: Wiesbaden, Germany
- September 9-14, 2001: Liège, Belgium
- May 5-10, 2002: Rome, Italy

The special session topics were:

- Treatment walls and permeable reactive barriers (Vienna)
- Monitored natural attenuation (Angers)
- Decision support tools (Wiesbaden)
- Performance validation of in situ remediation technologies (Liège)
- Monitoring and measurement (Rome)

This and many of the Pilot Study reports are available online at http://www.nato.int/ccms/ and http://www.clu-in.org/intup.htm. 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 presentations in this decision support tools report should be obtained from the individual authors.

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

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PROJECTS INCLUDED IN NATO/CCMS PHASE III PILOT STUDY

SUMMARY TABLE

		MEDIUM		**CONTAMINANT**					
PROJECT	COUNTRY	Soil	Groundwater	VOCs	SVOCs	Pesticides/PCBs	PHCs	Inorganics	NOTES
1. Bioremediation of Oil-Polluted Loamy Soil	Belgium	T			T		T		PAHs, munitions chemicals
2. Pilot Test on Decontamination of Mercury-Polluted Soil	Czech Rep.	T	T		T			T	Hg, metals, PAHs, TPH
3. Permeable Treatment Beds	Germany		T	T	T		T	T	PAHs, BTEX, TCE, PCE
4. Rehabilitation of Land Contaminated by Heavy Metals	Greece	T						T	Pb, Zn, Cd, As, H^+, $SO_4^=$
5. Application of BioScreens and Bioreactive Zones	Netherlands		T	T	T	T	T		Chlorinated pesticides, BTEX, TPH, HCH, PCE, TCE
6. Rehabilitation of a Site Contaminated by PAH Using Bio-Slurry Technique	Sweden	T			T			T	PAHs, cyanides, metals, ammonium compounds
7. Risk Assessment for a Diesel-Fuel Contaminated Aquifer Based on Mass Flow Analysis During Site Remediation	Switzerland		T				T		PHC
8. Obstruction of Expansion of a Heavy Metal/Radionuclide Plume Around a Contaminated Site by Means of Natural Barriers Composed of Sorbent Layers	Turkey	T	T					T	Pb, As, Cr, Cu, Cd, Hg, Ni, Zn; ^{137}Cs, ^{90}Sr, ^{238}U
9. Solidification/Stabilization of Hazardous Wastes	Turkey	T			T	T		T	PCBs, AOX, metals
10. Metal-Biofilms Interactions in Sulfate-Reducing Bacterial Systems	UK		T					T	Metals (Cu, Zn, Cd), radionuclides (Lab-scale)
11. Predicting the Potential for Natural Attenuation of Organic Contaminants in Groundwater	UK		T	T	T		T	T	Coal tars, phenols, creosol, xylenols, BTEX, NH_4^+
12. Treatability Test for Enhanced In Situ Anaerobic Dechlorination	USA		T	T	T				TCE, DCE, VC, PCE
13. Permeable Reactive Barriers for In Situ Treatment of Chlorinated Solvents	USA		T	T				T	PCE, TCE, DCE
14. Thermal Cleanup Using Dynamic Underground Stripping and Hydrous Pyrolysis/Oxidation	USA	T	T	T		T			PAHs, fuels, gasoline, chlorinated solvents, pentachlorophenol

		MEDIUM		CONTAMINANT					
PROJECT	COUNTRY	Soil	Groundwater	VOCs	SVOCs	Pesticides/PCBs	PHCs	Inorganics	NOTES
15. Phytoremediation of Chlorinated Solvents	USA		T	T					TCE, TCA, DCE, PCE, xylenes, methyl chloride, TMB
16. In-Situ Heavy Metal Bioprecipitation	Belgium		T					T	Heavy Metals (Zn, Cd, As, Pb, Cr, Ni, Cu, sulfate)
17. GERBER Site	France	T	T	T	T	T		T	Chlorinated solvents, BTEX, PCBs, phenols, phthalates, Pb, Zn
18. SAFIRA	Germany		T	T					Complex contamina-tion, chlorobenzene
19. Successive Extraction – Decontamination of Leather Tanning Waste Deposited Soil	Turkey			T				T	Tanning wastes
20. Interagency DNAPL Consortium Side-by-Side Technology Demonstrations at Cape Canaveral, Florida	USA	T	T						DNAPLs
21. Development and Use of a Permeable Adsorptive Reactive Barrier System for Ground Water Clean-up at a Chromium-Contaminated Site	Switzerland		T					T	Chromium (VI)
22. Thermal In-Situ Using Steam Injection	Germany	T		T					TCE, BTEX
23. Bioremediation of Pesticides	USA	T				T			Chlordane, DDT, DDD, DDE, dieldrin, molinate, toxaphene
24. Surfactant-Enhanced Aquifer Remediation	USA		T	T					PCE
25. Liquid Nitrogen Enhanced Remediation (LINER)	Netherlands		T	T					Chlorinated hydrocarbons
26. SIREN: Site for Innovative Research on Monitored Natural Attenuation	UK		T	T					Organic solvents
27. Hydro-Biological Controls on Transport and Remediation of Organic Pollutants for Contaminated Land	UK	T	T	T	T				PAHs, phenols, substituted benzenes
28. Demonstration of a Jet Washing System for Remed-iation of Contaminated Land	UK	T					T		Tars, petroleum hydrocarbons
29. Automatic Data Acquisition and Monitoring System for Management of Polluted Sites	Italy	T	T	T					TPH, BTEX

30. Biological Treatment Technologies for the Cleanup of TNT-Contaminated Sites	Germany	T							TNT
31. Phytoremediation Evaluation for Petroleum Hydrocarbons in Surface Soil	USA	T			T		T		Petroleum, PAHs
32. Remediation of Chlorinated Solvents in Groundwater by Chemical Reduction Using Zero-Valent Iron, Pneumatic Fracturing, and Reagent Atomization	USA		T	T					TCE
33. Chemical Oxidation and Natural Attenuation at the Camden County Landfill	USA		T	T					Chlorinated ethenes

KEY:

AOX = adsorptive organic halogens
BTEX = benzene, toluene, ethylbenzene, and xylenes
DCE = dichloroethene
HCH = hexachlorocyclohexane
PAHs = polycyclic aromatic hydrocarbons
PCBs = polychlorinated biphenyls
PCE = tetrachloroethene
PHCs = petroleum hydrocarbons
SVOCs = semivolatile organic compounds
TMB = trimethylbenzene
TCA = trichloroethane
TCE = trichloroethene
TNT = trinitrotoluene
VC = vinyl chloride
VOCs = volatile organic compounds

Project No. 1

Bioremediation of Oil-Polluted Loamy Soil

Location	**Project Status**	**Media**	**Technology Type**
"van Oss" site, former fuel storage depot, Neder-Over-Heembeeck	Interim Report	loamy soil	bioremediation
Technical contact Ecorem nv Dr. Walter Mondt ir. Serge Van Meerbeeck Wayenborgstraat 21 2800 Mechelen Tel: 015/29.49.29 Fax: 015/29.49.28 E-mail: Ecorem@glo.be	**Project Dates** accepted 1994 final report 1997	**Contaminants** mineral oil	
	Costs Documented? yes	**Project Size** full-scale (proposed future pilot project)	

The information in this project summary is current as of January 2002.

1. INTRODUCTION

Name of the technology: Bioremediation of oil polluted loamy soil.

Status of the technology: Highly innovative and reasonable costs. Further experiments are required to evaluate different bioremediation techniques for the decontamination of loamy soil.

Project Objectives: Decontamination of oil polluted loamy soil by an in-situ activated biorestoration system, composed of a bioventing and a biostimulation system.

Following the good decontamination results on the van Oss site, this project is considered as a first step towards a more general and more effective application of bioremediation of contaminated loamy soils. In collaboration with the ULB (Université libre de Bruxelles) Ecorem proposed a pilot project to NATO, with objective to examine which bioremediation techniques could efficiently be used in the decontamination of loamy soils polluted with hydrocarbons.

2. SITE DESCRIPTION

The van Oss site is a former fuel storage depot in Neder-over-Heembeek, contaminated with mineral oil. A topographical situation of the site is shown on Figure 1.

3. DESCRIPTION OF THE PROCESS

Based upon a reconnoitring soil examination, it was proven that the soil as well as the groundwater of the former fuel storage depot van Oss was seriously contaminated with mineral oil. Compared to the contamination with this parameter, the presence of other components present was negligible.

The volume of contaminated soil (unsaturated zone) was estimated, based on the reconnoitering soil examination, at 3.500 m³. Proceeding with these data, selective excavation of the contaminated zones was a first option to be considered.

In order to draw up a detailed proposal for decontamination, Ecorem proposed an elaborated analysis campaign based on a sample grid.

Based on the analytical results and the positioning of the grid the volume of contaminated soil was assessed. Table 1 gives an overview of the volumes of contaminated soil. In Figure 3 the horizontal spreading of the mineral oil contamination in the soil is represented.

Table 1: Overview of the volumes of contaminated soil (mineral oil)

	>525mg/kg DES	*>1000 mg/kg DS*	*>5000mg/kg DS*
Depth (cm)			
0-200	9231 m^3	6284 m^3	943 m^3
	14,770 tons	10,054 tons	1509 tons
0-250	10,997 m^3	6997 m^3	1050 m^3
	17,995 tons	11,196 tons	1680 tons
0-300	12,763 m^3	7711m^3	1156 m^3
	20,420 tons	12,338 tons	1850 tons

The cubing shows that the volumes of contaminated soil were considerably higher than estimated at first. As a result, Ecorem proposed an alternative decontamination technique, i.e., an in-situ activated biorestoration system composed of a bioventing and a biostimulation system. Bioventing consists of a forced air flushing of the unsaturated soil with as main objective the supply of oxygen in order to stimulate the biodegrading activity of the microorganisms present in the soil. The biostimulation in this project consisted of mixing the contaminated ground with compost and wood flakes, in order to obtain a porous matrix, and the addition of nutrients to enhance microbial activity.

Decontamination of the unsaturated zone consisted of the following stages:

A. Excavation of the Hot Spots

Hot spots (areas with severe contamination - here areas where the concentration of mineral oil >5000mg/kg DS) are secondary sources of contamination, and can therefore inhibit the efficient functioning of an in-situ decontamination technique. It is thus essential that these secondary sources of contamination be removed, for the in-situ decontamination technique to have any chance of success.

B. Biodegradation

The efficiency of the biodegradation system strongly depends on soil characteristics. In order to obtain a good biological degrading, the oxygen level and level of nutrients need to be established in optima forma.

A good supply of oxygen can only be realised in porous soils. Soils with limited air permeability, such as loamy soils, therefore need to be mixed with structure amelioration additives. Oxygen is necessary for hydrocarbon degradation, as this is done aerobically. Oxygen limitation leads to slowing down and discontinuing of the degradation kinetics. The creation of good air permeability is also of crucial importance for the bioventing.

A second parameter, the nutrient supply is just as essential for a good biodegradation. In order to optimise the feeding pattern the soil should be mixed with bioactivating substrates.

C. Soil Air Extraction

The efficiency and the design of the soil air extraction strongly depend on the soil characteristics, as these have an important effect on the movement and transportation of soil air (gas). The most important determining soil characteristics are: soil structure, stratigraphy, porosity, grain size, water level, residual contamination, and presence of macro pores.

The air permeability of the soil represents the effect of these different soil characteristics. The air permeability indicates to what extent fumes can float through a porous environment.

Air permeability and airflow velocity are linearly dependent. The higher the air permeability and the airflow velocity, the greater the chances of an effective soil air extraction.

Taking into account that the loamy/clayey unsaturated zone at the van Oss site is heterogeneously built, the air transportation throughout the soil is prevented and the airflow velocity is relatively small. A solution to break this heterogeneity was to mix this oil with structure-enhancing additives till the depth of 0.5 m above ground water level. This also enlarged the porosity of the soil, which was favourable for air transportation.

In order to get a large zone of influence, the placement of horizontal injection and withdrawal drains was chosen. Placement of drains was performed in layers, the soil mixed with structure-enhancing additives being completed (Figure 2)

The withdrawn air was purified in an air treatment establishment, consisting of following units:

Air/Water Separator and Air Filter

This separator and filter eliminates soil damp (water) and fine particles that may damage the mechanical equipment, and might disrupt further air treatment. The water discerned needs to be collected and, if contaminated, purified.

Vacuum Pump

The vacuum pump causes the suction in the underground. The compression heat in the pump causes a temperature increase and a corresponding decrease of the relative humidity of the airflow when leaving the blower.

Air Cleaning Unit

The pumped up air was treated by means of biofiltration and active carbon filtration.

Measure Devices

By measuring the different parameters the air treatment and soil air extraction could constantly be monitored and adjusted.

The above mentioned decontamination concept has a double advantage:

- It avoids transportation of considerable volumes of contaminated soil (approx. 12.000 tons with a concentration higher than 1000mgkg DM) to an adapted dumping-ground;
- It relocates the problem of the desired quality from a problem of volume to a problem of time. The final quality of the soil is function of the time period in which the system is applied.

The complete decontamination setting is represented in Figure 2.

4. RESULTS AND EVALUATION

The bioremediation of the unsaturated zone was started in October 1995, after the hot spots had been excavated and the remaining soil had been mixed with compost and wood flakes. After two months a first analysis campaign was executed. The results have been visually represented in Figure 3. Further analysis campaigns were executed after 5 and after 10 months. These results have been represented in Figure 4 and Figure 5. Based on the visual representation of the horizontal spread of the contamination in the different figures it has become clear that the bioremediation technique is successful.

After ten months the mean concentration of mineral oil was less than 490 ppm, while the decontamination objective imposed by the BIM was a concentration of 900 ppm.

From these results it is clear that bioremediation techniques can be efficient on loamy soil on short term, so that further examination for possible bioremediation techniques on finer textures offers quite a lot of perspective.

5. COSTS

The bioremediation technique was also a favourable concept regarding the cost of decontamination. The total cost for bioremediation of the unsaturated area amounted to about 20 million franks. A selective excavation of the contaminated grounds would have easily exceeded a 30 million franks' cost price.

6. PROPOSAL OF A PILOT PROJECT ON BIOREMEDIATION OF LOAMY SOIL

Following the decontamination at the van Oss site, Ecorem proposed to NATO a pilot project, with objective to verify which bioremediation techniques are effective in the decontamination of contaminated loamy soils.

In order to dimension the different technologies to be tested in the scope of this pilot project, the following activities are planned prior to the experimental stage:

Characterization of the Soil to be Treated

This stage consists of the analysis of the soil to be treated, regarding the most relevant organic and inorganic parameters. Therefore, a number of samples will be taken. A good characterisation is necessary because certain pollutants, even in low concentrations, have a certain inhibiting effect on the microbial activity. Complementary to these analyses a certain number of general parameters such as grain size, the C/N relation and the degree of humidity will be determined as well.

Determination of Initial Microbial Activity

The determination of initial microbial activity is performed based on the classical techniques used in soil microbiology, such as microscopical research (countings), determination of the biomass by fumigation and extraction, respiration measurements (CO_2 production) and ATP determinations.

Determination of the Maximum Potential Biodegradability of the Contamination Present

In order to determine the maximum degradability of the pollutants, column tests with lysimeters are being executed. Therefore optimal conditions for microbial growth and degradation are created by means of addition of water, nutrients, air, microorganisms and other additives. During the column tests the pollutant concentration, the use of oxygen and the CO_2 production are continuously monitored in order to obtain an accurate image of the biodegradability of the pollutants.

The preparatory stages will result in a first indication of the potential applicability of bioremediation as a decontamination technique for loamy soils that were contaminated with hydrocarbons.

Based on the results and conclusions of the preparatory stages a number of decontamination concepts and configurations will be tested on a lab scale. Regarding the in-situ decontamination techniques, this is only executed with the help of column studies based on soil column lysimeters. Regarding the ex-situ decontamination techniques, mainly bioreactor tests will be executed.

Soil column lysimeters are simple but efficient means to verify the possibilities to what extent the soil can be in-situ decontaminated with the help of bioremediation techniques. In Figure 6 a schematic representation of the test setting is given. Different soil columns are being equipped as represented in Figure 6. In the test setting fluid solutions can be put in with the help of a time-directed system that is established on top of each column. Furthermore, air fumes can be added in each column. Before entering the column, the fumes are lead through a shaft filled with glass pearls to enable a uniform separation. Different column tests will be performed simultaneously to monitor the microbial activity and the evolution of the contaminants under different circumstances and feedings. The liquid solutions will mainly consist of nutrient mixtures containing nitrogen sources, phosphates and oligo-elements. For each column the effluent is collected and analysed on pH, conductivity and nutrient concentrations. In order to measure microbial activity in the column, the production of CO_2 produced is determined. On the columns following treatments will be performed: control setting without specific treatment; only addition of water, addition of water and nutrients, addition of water + nutrients + microorganisms; addition of water + air + nutrients; addition of water + microorganisms + air + nutrients.

Such soil column lysimeters are extremely well equipped to verify whether contaminated sites can be decontaminated in-situ with the help of bioremediation techniques. In addition, the column tests will be used for the evaluation of ex-situ decontamination techniques, during which the contaminated soil will be submitted to different preliminary treatments (e.g., mixing with compost). Different compost formulas and relationships in the process will be tested.

Based on the results of the experiments on a lab scale, the most appropriate concepts will be tested on a larger scale, in order to obtain a more realistic idea. Therefore the ex-situ decontamination techniques will be tested in the soil-recycling centre. Regarding the in-situ decontamination techniques, the different contaminated zones in different sites will be isolated civil-technically in order to prevent a horizontal spreading of the contamination. The volume of isolated cells will amount to approximately $50m^3$. In order to prevent spreading towards the ground water, a pump and injection system are established around different cells. If possible slots will be dug to the depth of 2 to 3 m around the cells. From these slots horizontal perforated tubes will be installed under the cells to enable monitoring of the groundwater as well as of the soil vapour. With this sampling system the heterogeneity of the soil can be optimally studied.

This decontamination experiments will be conducted on the future soil-recycling centre of s.a. Ecoterres in Brussels. This centre will be built on the van Oss site, owned by the G.O.M.B. Figure 7 gives an impression of the future soil-recycling centre.

Figure 1:

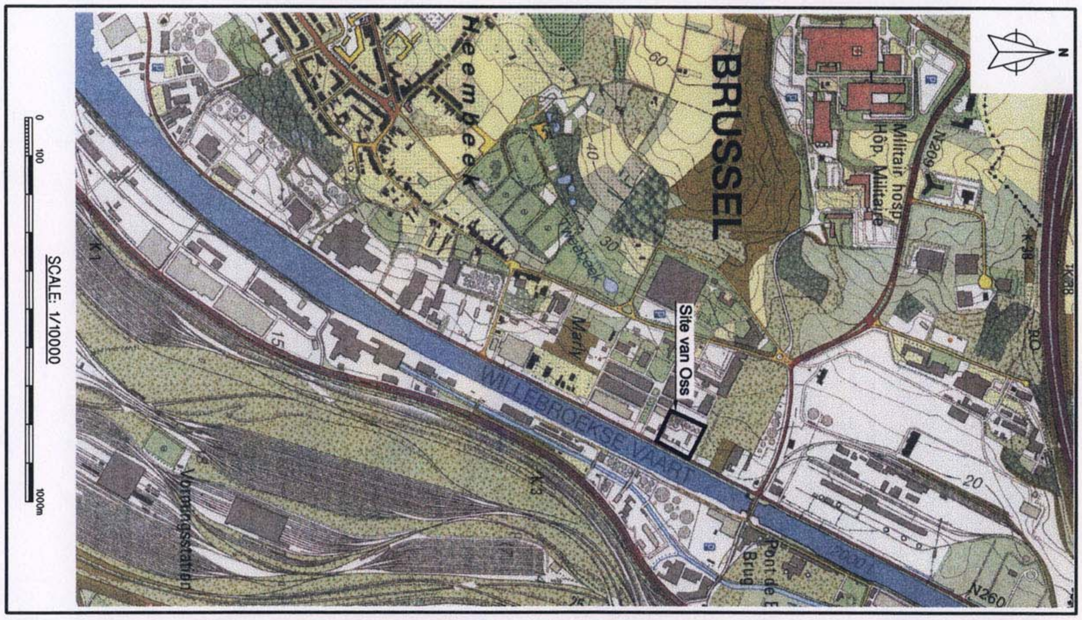

FIG. 1: LOCATION OF "SITE VAN OSS" ON THE TOPOGRAPHICAL MAP

F039 F-1001-00

Figure 2:

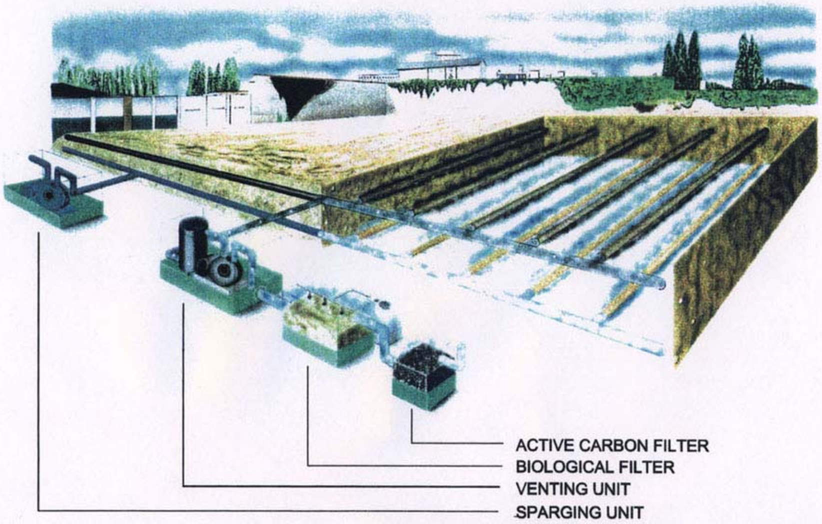

FIG. 2: LAY-OUT OF THE SANITATION ARRANGEMENT

F039 F-1002-00

Figure 3:

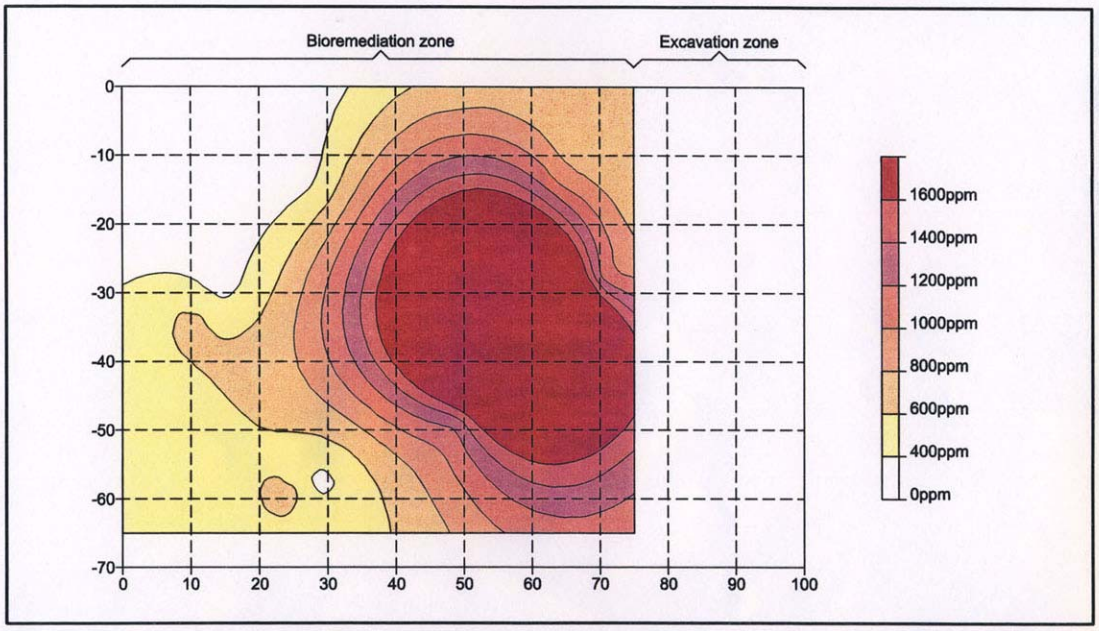

FIG.3:DISPERSATION OF HYDROCARBONS AFTER 2 MONTHS OF BIOREMEDIATION
(concentration of hydrocarbons in mg/kg DM)

F039 F-1003-00

Figure 4:

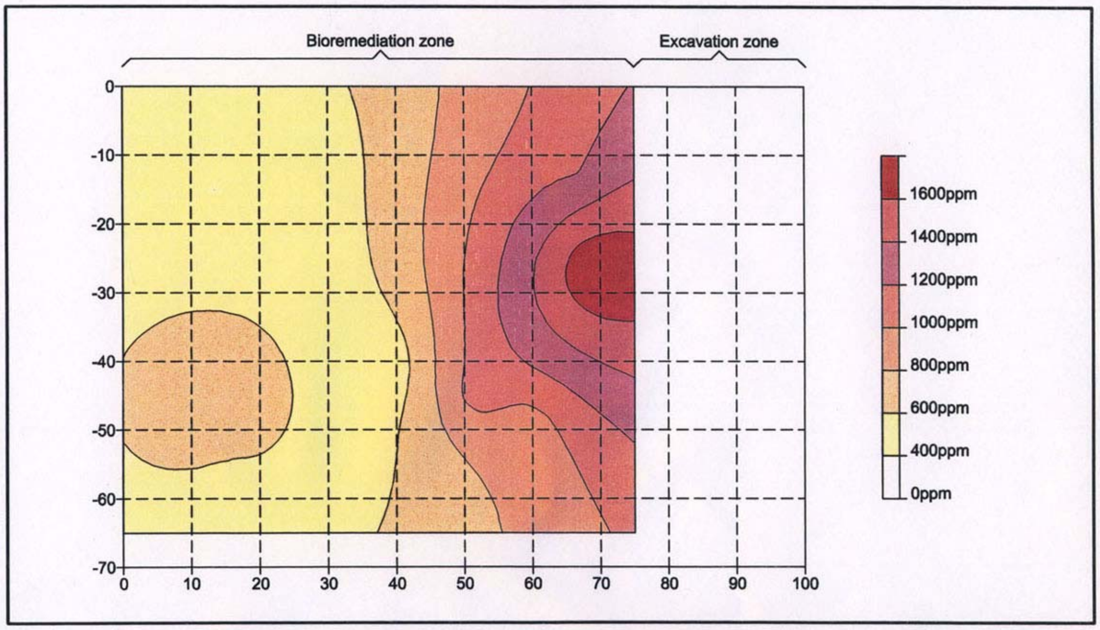

FIG.4: DISPERTION OF HYDROCARBONS AFTER 5 MONTHS OF BIOREMEDIATION
(concentration of hydrocarbons in in mg/kg DM)

F039 F-1004-00

Figure 5:

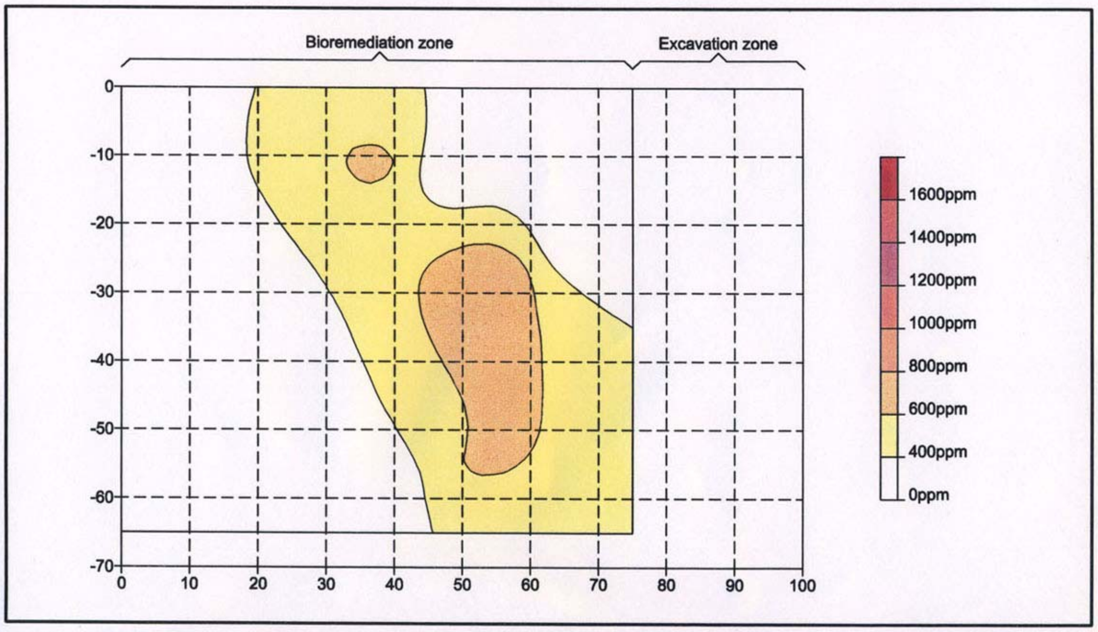

FIG.5: DISPERTATION OF HYDROCARBONS AFTER 10 MONTHS OF BIOREMEDIATION (concentration of hydrocarbons in mg/kg DM)

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Figure 6:

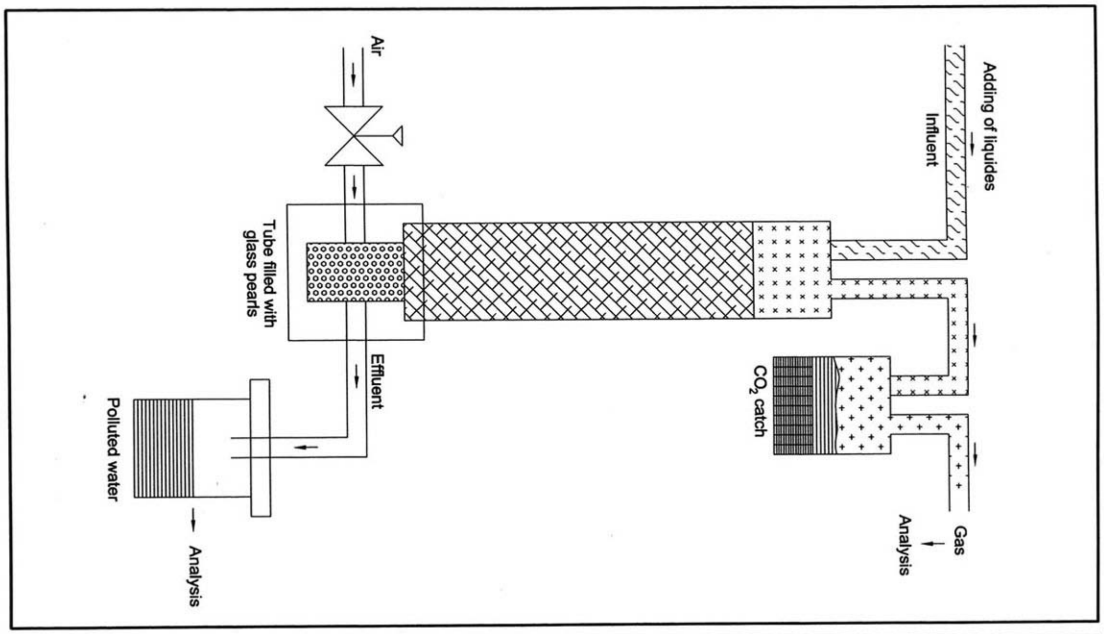

FIG.6: SCHEME OF TESTING LINE-UP

Ecorem

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Figure 7:

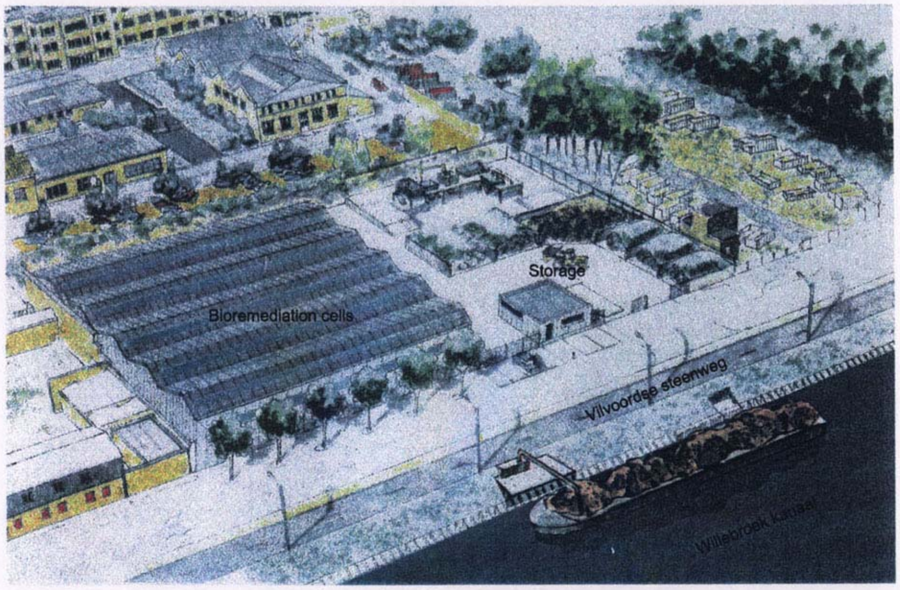

FIG.7: IMPRESSION OF THE FUTURE SOIL REMEDIATION CENTER

Environmental consulting, remediation, engineering and management
Ecorem

F039

F-1007-00

<table>
<tr><td colspan="4">Project No. 2
Pilot Test on Decontamination of Mercury-Polluted Soil</td></tr>
<tr><td>Location
Spolchemie a.s.,
Ústí nad Labem,
Czech Republic</td><td>Project Status
Final report</td><td>Contaminants
Metallic mercury</td><td>Technology Type
Wet gravity separation</td></tr>
<tr><td rowspan="2">Technical Contact
Marek Stanzel
KAP, Ltd.
Trojská 92
171 00 Prague 7
Czech Republic
Tel: (00-420-2) 83 09 06 14
Fax: (00-420-2) 83 09 06 58
E-mail: m.stanzel@prg.kap.cz</td><td>Project Dates
Accepted
1999
Final Report
2000</td><td colspan="2">Media
Soil</td></tr>
<tr><td>Costs Documented?
Yes</td><td>Project Size
Pilot test - 1 m³ (2 tons)</td><td>Results Available?
No</td></tr>
</table>

Project 2 was completed in 2000.

1. INTRODUCTION

The pilot test on decontamination of mercury-polluted soil consisting of excavation of mercury-polluted soil and on-site wet gravity separation was conducted at the area of Spolchemie located in the center of the city Ústí nad Labem in northwest Bohemia. The pilot test was conducted with the aim to demonstrate the recovery efficiency and possibility to fulfill the objective limit for decontamination, i.e., 70 ppm of Hg in treated soil.

2. BACKGROUND

In 1998, the investigation of pollution and risk assessment was finished in the area of Spolchemie, a large chemical plant located in the center of Ústí nad Labem in northwest Bohemia. High-grade elemental Hg pollution of soil was found in areas adjacent to former and current buildings of the mercury-cell process for producing caustic soda, caustic potash, hydrogen, and chlorine. Maximum concentrations of mercury often reach up to hundreds of thousands ppm. Total calculated amount of metallic Hg is 267-445 tons in 222.740 m^3 of polluted soil. The mercury is present in the form of visible drops or softly dispersed in the soil. The scale and character of the pollution was presented in detail in previous papers. A scale of the cleanup project has not been decided yet, but it looks very probable that the main volume of polluted soil will be excavated and decontaminated and the lower level of pollution will be monitored only. The feasibility study evaluating decontamination methods used worldwide was performed.

Because of a lack experience in decontamination of mercury-polluted soils in the Czech Republic, a project was conducted in 1998 for identification and laboratory tests for decontamination. The project aimed to select the most suitable method for decontamination of soils with massive pollution by mercury. For a large quantity of contaminated material the thermal method (used worldwide) is not considered suitable for our case because of high-energy costs. Regarding the laboratory tests, the experts of KAP decided to solve this problem by means of wet gravity separation, taking advantage of mercury's specific physical and chemical properties. On the basis of laboratory tests, the Pilot Test Project for Decontamination of Mercury-Polluted Soil was elaborated and accepted in 1999.

The main aim and tasks of the pilot test was to solve the following problems in semi-industrial scale:

- to check recovery efficiency of the proposed gravity separation on 1 - 3 m^3 of polluted material;
- to check possible adsorption of Hg on clay minerals and its influence on the decontamination efficiency;

- to test the dewatering of treated material;
- to specify the energy consumption and total costs of decontamination;
- to design the optimal decontamination unit that could be maintained and operated effectively under the conditions of the local economy and infrastructure.

The Pilot Test was funded by the Czech National Property Fund. The total cost was 0.5 M CZK (13,000 USD).

3. TECHNICAL CONCEPT

The decontamination unit set up for the pilot test consists of the following devices:

steel container— excavated material was loaded into steel container where the material was blunged by
hydromonitor— this device blunges and feeds the treated material to
gravity storage bin— from this tank the suspended material was pumped to
hydrocyclone— the first stage of separation - classifying into two fractions - mud and sand (in this fraction, the metallic mercury is concentrated and the mud is dewatered and backfilled into the excavation hole)
centrifugal concentrator— the second stage of separation, the pre-concentrate is finally treated
sedimentation basins— wastewater from hydrocyclone and centrifugal concentrator is pre-treated (sedimentation of mud)
centrifuge— dewatering of mud from hydrocyclone and sedimentation basins.

During the processing of polluted soil the important points of tested technology was sampled:

polluted soil— this represents a problem because of the highly variable Hg concentration in the material (due to occurrence of Hg in drops and/or finely disseminated), analyzed concentrations vary from X00 to 120,000 ppm in the feed (i.e., polluted soil);
waste from hydrocyclone (mud) — determined values of Hg concentration did not exceed 10 ppm;
pre-concentrate from hydrocyclone (sandy fraction) — due to high specific weight of Hg it is also complicated to collect representative samples;
waste from centrifugal concentrator— due to high specific weight of Hg it is also complicated to collect
representative samples— determined Hg concentration was in order X ppm;
concentrate, i.e., separated mercury— this output was not sampled because it is represented by metallic mercury with admixture of sand, in frame of conducted Pilot Test about 9 ml of mercury (i.e., approximately 121.5 g) was separated.
process water— determined concentration of Hg were under the detection limit (<0.003 mg/L) so during the decontamination process the Hg does not dissolve in processing water.

The test for dewatering of treated soil was successful. The determined moisture in treated soil shows that it is possible to backfill this material into the excavation because the moisture in dewatered material is only about 5% higher than in natural soil.

4. ANALYTICAL APPROACH

During the pilot test, the excavated material, feed, and outputs were sampled and analyzed for mercury concentration, as well as the process water. The total concentration of Hg, as well as the concentration of metallic, organic, and inorganic form of Hg, was analyzed. The concentration of accompanying pollutants was also monitored (i.e., CHCs, heavy metals). Analyses were carried out in accredited laboratories by relevant analytical methods.

5. RESULTS

The conducted pilot test approved the excellent recovery efficiency of wet gravity separation of the mercury from polluted soil. Concentration of mercury in the feed reached values over 100,000 ppm. Analyzed concentration in output (i.e., treated "clean" soil) did not exceed 10 ppm (i.e., in conditions of The Bohemian Massif value only slightly exceeding the natural background).

On the basis of results of the pilot test a final proposal on decontamination of mercury polluted soil was elaborated. Proposed treating technology is consisting of accessible technology.

6. HEALTH AND SAFETY

Regarding the mercury's specific physical and chemical properties and wet treating process, no extraordinary personal protection clothing or devices were used.

7. ENVIRONMENTAL IMPACTS

Conducted pilot test had no impact on the environment. Treated (i.e., clean) soil was backfilled into the space of excavation. Process water was pre-treated in sedimentation basins and released to the plant's sewerage system and subsequently to the wastewater treating plant. The quality of both treated soil and wastewater was monitored. Content of metallic mercury in treated soil was below 10 ppm. Concentration of Hg in wastewater was under the detection limit (<0.003 mg/L).

8. COSTS

The total project cost was 0.5M CZK (13,000 USD). The cost breakdown was as follows:

Personnel cost (managing, supervision, consultant) - 49%
Pilot Test operation (excavation, treating, dewatering, sampling) - 41%
Laboratory cost -7%
Transportation - 2%
Miscellaneous - 1%

9. CONCLUSIONS

In the frame of the successfully conducted pilot test, the mercury contaminated soil was excavated and blunged, and by the means of gravity separation the mercury was recovered. Treated soil was dewatered by centrifuge. During the pilot test all the feed and outputs, as well as processing water, were sampled and analyzed.

The pilot test approved excellent recovery efficiency of wet gravity separation of metallic mercury using normally accessible technology. On the basis of the results, the proposal on gravity decontamination technology for remediation in the area of Spolchemie was elaborated. This proposal is assessed by The Czech Environmental Inspectorate.

10. REFERENCES

1. Sedláček M.: Risk Analysis Update - Pollution of Rock Environment and Groundwater by Mercury in the Area of Spolchemie a.s. in Ústí nad Labem. KAP, Ltd., Prague, 1998.

2. Sedláček M.: Report on Laboratory Testing of Decontamination of Mercury Polluted Soil., KAP, Ltd., Prague, 1999.

3. Sedláček M.: Report on Pilot Test on Decontamination of Mercury Polluted Soil. KAP, Ltd., Prague, 2000.

Project No. 3 **Permeable Treatment Beds**			
Location Former solvent blending plant, Essen, Germany	**Project Status** Interim Report, Field Tests finalized	**Contaminants** Chlorinated and non-chlorinated solvents, BTEX-aromates, TCE, PCE	**Technology Type** Permeable reactive barrier as in situ groundwater remediation technology
Technical Contact Eberhard Beitinger WCI Umwelttechnik GmbH Sophie-Charlotten-Straße 33 14059 Berlin Tel: +49-/(0)30-32609481 Fax: +49-(0)30-32609472 E-mail: exbeiti0@wcc.com	**Project Dates** Accepted 1997 Completed 1999	**Media** Groundwater	
	Costs No, cost estimation available	**Project Size** Full-scale	**Results Available?** No, field test results available

Project 3 was completed in 1999. The project description was updated in November 2002.

1. INTRODUCTION

This on-site remedial demonstration project will be conducted at an old solvent blending plant in the subburben area of the city of Essen. The downstream plume of heavily contaminated groundwater will be treated by an innovative permeable reactive barrier (PRB) technology. Advancing the full-scale project a field test was conducted to evaluate the adsorption capacity of the filling material (activated carbon) and the performance time of a single filling. Project objectives are to learn about implementation of the wall structure and long-term efficiency of the fillings regarding in-situ treatability of groundwater by passing the barrier.

2. BACKGROUND/SITE DESCRIPTION

From 1952 to 1985 a chemical factory was situated on an area of about 10,000 m² located in a city in the Ruhr area. Mostly solvents like hydrocarbons, volatile chlorinated hydrocarbons, PAHs, petroleum, terpentine oil substitute, ketones, monoethyleneglycol and alcohols were handled, stored and processed. Today a residential building is left on the site while underground and above ground tanks are demolished.

The ground was filled up 2,0 m over silty soil (approx. 4 to 11 m thick). Below the silt a layer of sand and gravel (0.8 to 7.4 m) and marly sands (7.0 to 16.3 m below the top) have been detected. The marly sands are the first waterproof layer.

The First aquifer is about 1.0 to 3.2 m thick and the flow velocity is very slow. The following coefficients of permeability exist:

- first aquifer: $k_f = 6.6 \cdot 10^{-6}$ m/s
- waterproof layer: $k_f = < 10^{-7}$ m/s

The groundwater surfaces in the North of the site in a little source. Due to this emission the surface water in a small creek downstream the source is contaminated.

The concentrations of main contaminants in groundwater are petrol hydrocarbons 23.6 mg/L to 164.0 mg/L, volatile chlorinated hydrocarbons 27.0 mg/L and aromatic hydrocarbons 153.0 mg/L. Furthermore higher concentrations of manganese and iron are present.

The project is funded by the city of Essen and the state Nordrhein-Westfalen as the former owner got bankrupt.

3. DESCRIPTION OF THE PROCESS

Three alternatives of permeable treatment wall types have been developed and evaluated by WCI for specific site conditions. Regarding construction costs, treatment efficiency and ground-water control, alternative 2 has been evaluated best. This alternative consists of a short treatment wall section of 35 m length with additional vertical barriers along the two endings of the treatment bed. So a total width of the plume to approximately 145 m is covered. The ground-water will be directed to the treatment section and contaminants will be recovered by adsorption.

A permeable reactive barrier is a passive in-situ treatment zone of reactive material that degrades or immobilises contaminants as groundwater flows through it. Natural gradients transport contaminants through strategically placed treatment media. The media degrade, sorb, precipitate, or remove dissolved organics, metals, radionuclides, and other pollutants.

WCI-Umwelttechnik GmbH, the Germany subsidiary of woodward-clyde has developed and patented a barrier construction system which allows the removal of used reactive material and the refill of fresh media without destroying or rebuilding the wall system. This design will enable potential users to operate the Treatment Barrier for a long period, up to several decades, without severe reduction of effectively. The permeable wall construction can be installed in open trenches down to 10 or more meters. The system includes filter layers to prevent losses of hydraulic capacity by fine soil particles, a permanent open space for the reactive material as well as measures to control effectiveness and to monitor the groundwater quality.

In comparison with pump-and treat methods to clean groundwater contaminations, the passive permeable reactive barrier concept is technically sound and in most cases less expensive to install. Operation costs are very low and limited to monitoring due to that no pumping of groundwater is necessary.

4. RESULTS AND EVALUATION

Installation of the PRB will be started in 1998 and performance evaluation will be executed in the following years by monitoring groundwater qualities and the remaining adsorption capacities of the filling material.

The results of the field testing with two carbon filter columns was conducted successfully in the second half of 1997. Both columns were operated under in-situ conditions regarding groundwater quality and contaminant concentrations. No problems with fines or precipitating iron or manganese have been detected during a five-month operation period. One column was operated to actual time conditions and the second with a much faster scale (1 month simulating 25 years of operation). The calculated operation time of one filling was a minimum of 30 years. Test results showed performance times up to 5 times longer. Also no negative effects by biological activity such as bio-clogging could be detected during the field testing.

These results will be presented to the relevant water authorities for their permission. After the permission process is finalised, the construction of the full-scale PRB will be started immediately.

5. COSTS

The costs for conducting the field tests have been DM 100.000,--. The overall costs to erect the wall system and the fill with activated carbon is estimated to be DM 1.500.000,--. Included are additional costs for monitoring the water quality for 30 years, which is a long as the minimum performance time of one single filling will be.

In comparison with traditional pump-and-treat groundwater remediation costs, the proposed permeable reactive barrier system will be at least 25 % less expensive.

6. REFERENCE

1. Eberhard Beitinger, and Eckart Bütow. *Machbarkeitsstudie zum Einsatz einer Adsorberwand – „Schönebecker Schlucht“ in Essen*, Internal Report, WCI, Wennigsen, 1997 (not published)

2. Eberhard Beitinger, and Eckard Bütow. *Abschlussbericht zur Durchführung von Pilotversuchen für eine geplante Adsorberwand - „Schönebecker Schlucht“ in Essen*, Internal Report, WCI, Wennigsen, 1998 (not published)

<table>
<tr><td colspan="4">Project No. 4
Rehabilitation of Land Contaminated by Heavy Metals</td></tr>
<tr><td>Location
Lavrion, Kassandra (Greece)
Sardinia (Italy)
Estarreja (Portugal)</td><td>Project Status
Final Report</td><td>Contaminants
Lead, zinc, cadmium, arsenic, acidity, sulfates</td><td>Technology Type
Alkaline additives
Surface barriers
Chemical fixation and immobilization
Soil leaching</td></tr>
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Tel: +30/1-772-2176
Fax: +30/1-772-2168</td><td>Project Dates
Accepted 1997
Final Report 2002</td><td colspan="2">Media
Mining tailings and waste rock, Pyrite cinders, Carbonaceous tailings, Soil</td></tr>
<tr><td>Costs Documented?
Yes</td><td>Project Size
Laboratory, Demonstration-scale</td><td>Results Available?
Yes</td></tr>
</table>

Project 4 was completed in 2002.

1. INTRODUCTION

Polymetallic sulphide mining and processing operations result in the generation of millions of tons of mining, milling and metallurgical wastes, most of them characterized as hazardous. Improper environmental management in the past, but to some degree in current operations, has resulted in intensive in terms of concentration and extensive in spatial terms pollution of land and waters by heavy metals and toxic elements, which migrate from the wastes. The project aims at developing (a) innovative, cost-effective and environmentally acceptable industrial technologies for the rehabilitation of land contaminated from sulphide mining and processing operations and (b) an integrated framework of operations that will allow for environmentally sustainable operation of the mining and processing industries.

Rehabilitation technologies investigated include:

Preventive

- Application of alkaline additives to prevent acid generation from sulfidic wastes.
- Formation of surface barriers with bentonite, zeolite or other additives to prevent pollutant
- migration from the pyrite cinders and calamina residues.
- Chemical stabilization of the heavy metals in situ in oxidic wastes and soils.

Remedial

- Removal of heavy metals from soils by leaching techniques.

The status of the technologies is bench and demonstration scale. *One particular technology involving the application of ground limestone to inhibit acid generation has been applied in full-scale for the rehabilitation of a 150,000 t/2,500 ha sulfidic tailings dam in Lavrion.*

2. SITES

The research is of a generic nature and the results applicable to a wide number of cases. The sites examined as case studies are given below:

Site	Description	Material tested
Lavrion, GR	Redundant polymetallic sulfide mine (argentiferous, galena, sphalerite, pyrite)	Sulfidic and oxidic tailings, soils
Stratoni, GR	Active polymetallic sulfide mines (galena-sphalerite-pyrite) with a mining history of more than 2.500 years.	Waste rock
Montevecchio, Monteponi, Sardinia, IT	Extensive Pb-Zn historic mining area. Currently, there is one operating and many redundant mines.	Sulfidic tailings, calamina red mud, soils
Estarreja, PT	Chemical industrial site. Production of sulfuric acid by roasting of pyrites in the period 1952-1991.	Pyrite cinders

3. DESCRIPTION OF THE PROCESSES-RESEARCH ACTIVITY

3.1 Preventive Technologies to Inhibit the Spread of Pollution from the Active Sources

Processes for the *prevention* of pollutant migration, which were investigated in laboratory scale and evaluated in field scale, include:

A. Limestone or Fly Ash Addition to Prevent Acid Generation from Sulfidic Wastes

The technical objective was the development of a process for the inhibition of acid generation from sulphidic wastes by making beneficial use of the oxidation-dissolution-neutralisation-precipitation reactions so as to achieve: on a microscale, precipitation of reaction products around the pyrite grains, inhibiting further oxidation and/or on a macroscale, formation of a hard pan that will drastically reduce the permeability of wastes to water and oxygen. By achieving these goals, the required limestone or other alkaline additive will be only a fraction of the stoichiometric requirements, therefore, the cost of application will be significantly lower compared to the current practice of adding near-stoichiometric quantities.

An extensive laboratory kinetic testwork was carried out using limestone, a low cost and commonly found at mine sites alkaline material, and fly ash, a by product of Greek-lignite powered electricity plants with significant neutralization potential and cementitious properties. Kinetic tests using columns or humidity cells were carried out for a period of 270-600 days. After 270 days of operation a selected number of columns as well the humidity cells were dismantled and a detailed geotechnical and geochemical characterisation of the solid residues was performed.

Based on the laboratory test results, field tests were constructed in Lavrion and Stratoni, for the remediation of sulphidic tailings and waste rock respectively, which have been running for a period of thirty months.

B. Formation of Surface Barriers for the Pyrite Cinders and Calamina Residues

The technical objective was the development of a cost-effective process for the inhibition of the toxic leachate generation from these wastes by modification of the top surface layer with bentonite or bentonite-zeolite additives. The aim was to achieve very low permeability of the surface layer in order to inhibit water infiltration and subsequent leaching of contaminants.

The laboratory work performed included: a) selection of the stabilising agents (bentonites and/ or zeolites and/ or other materials) having certain properties (proper sediment volume, swelling index, yield, filtrate loss and high cation exchange capacity), b) short term leaching tests to preliminarily determine parameters including mode of application and addition rates of the stabilizing agents and c) lysimeter kinetic tests. Following laboratory testing, field scale tests were conducted to evaluate the performance of low permeability layers including: a) a sand-bentonite mixture to cover pyrite cinders at the Estarreja site, and b) an alumina red mud stabilised with gypsum and calamina red mud mixture to cover calamina residues and Montevecchio oxidic tailings.

C. Chemical Stabilization of Metals in Oxidic Wastes and Soils

The technical objective was to develop a process for the in-situ immobilization of heavy metals that exist in toxic and bioavailable speciations by transforming them into less soluble and bioavailable species using calcium oxyphosphates or other low cost additives. A number of stabilizing agents including phosphates, alumina red mud, fly ash, peated lignite and biological sludge were tested on Lavrion and Montevecchio oxidic tailings and soils by conducting pot experiments. Stabilization was examined by chemical extraction tests and verified by actual biological tests. Chemical extraction tests included toxicity characterization using the EPA-TCLP test and determination of the bioavailable-phytotoxic fraction using a combination of EDTA, DTPA and $NaHCO_3$ leaching tests. The biological tests involved plant growth tests using dwarf beans (*Phaseolus vulgaris starazagorski*) as plant indicator. The morphological parameters of the plants (root weight, leaf area, length and weight of aerial parts) were measured. Samples from the roots and leaves were collected for the determination of the metal concentrations. Based on the laboratory test results, alumina red mud stabilised with gypsum was proven to be a successful stabilising agent for Montevecchio soils and was tested under field conditions. On the other hand a mixture of phosphates and peated lignite was selected and is tested in field scale for the stabilization of Lavrion carbonaceous tailings and soils.

3.2 Development of Remedial Industrial Technologies for the Clean-up of Contaminated Sites

Remedial measures for rehabilitation of contaminated soils include removal of contaminants by either chemical or physical means with operations, which can be applied either in-situ or ex-situ. The technical objective is to develop process/processes for the removal of heavy metals from soils by leaching techniques.

Leaching Methods for the Clean-up of Contaminated Soils

The work performed comprised the following stages: a) evaluation of alternative leaching reagents, i.e. oxalic acid, acetic acid, citric acid, Na_2H_2EDTA, $Na_2CaEDTA$ and an acidic brine consisting of $HCl-CaCl_2$, b) development of two integrated leaching processes based on the use of $Na_2CaEDTA$ and $HCl-CaCl_2$ reagents, with the investigation of all the required treatment stages, i.e. removal of metals from the pregnant solution, regeneration of reagents for recycling, polishing of effluents for discharge etc., c) comparative evaluation of the above processes on representative soil samples from Montevecchio and Lavrion sites. The integrated $HCl-CaCl_2$ and $Na_2CaEDTA$ processes were also evaluated with column experiments, in order to define crucial operating parameters for the application of *heap leaching* techniques on Montevecchio (MSO) and Lavrion (LSO) soils.

4. RESULTS AND EVALUATION

4.1 Limestone or Fly Ash Addition to Prevent Acid Generation from Sulfidic Wastes

Mixing of the pyrite with limestone at rates corresponding to only 15% of the stoichiometric quantity was effective both in preventing the generation of acidic drainage and reducing the hydraulic conductivity. Furthermore, mixing of pyrite or Lavrion tailings with 18-20 % w/w fly ash resulted in the formation of a cemented layer that reduced the permeability by two orders of magnitude as compared with the control inhibiting the downward migration of acidic leachates. Based on the laboratory test results, field tests were performed in Lavrion. The field test area was divided into 4 quadrants of 100 m^2 (10 x 10 m) where the alkaline materials were homogeneously mixed with Lavrion tailings and applied either to the entire mass of tailings or only to the upper layers. Monitoring results of the field tests for a period of 30 months indicated that the drainage produced from the test pads involving limestone and fly ash addition to the upper layer of tailings was minimal (only 0.2 and 0.07% respectively of the total precipitation and irrigation volume). Referring to the Stratoni waste rock, the separation of the sulphide rich -4 mm size fraction and its placement after mixing with 14% limestone on top of the coarse was proven effective in preventing acid generation even under acidic conditions. Based on the laboratory results, four field test pads were constructed in the Stratoni site. The remediation scheme investigated involves separation of the fine from the coarse fraction, mixing of the fine fraction with limestone and placement of the mixture on top of the coarse fraction. The monitoring results obtained for a period of 30 months indicated that the investigated remediation scheme reduced significantly the drainage volume and improved the leachates quality. No water was collected from the test pad 4 consisting of successive layers of homogeneously mixed fine waste rock with limestone and coarse waste rock.

4.2 Formation of Surface Barriers for the Pyrite Cinders and Calamina Residues

Laboratory tests showed that mixing of pyrite cinders or calamina red mud with bentonite would not reduce drastically the hydraulic conductivity, so that to achieve the formation of a low permeability layer, i.e. k: $\leq 10^{-7}$ cm/sec. Alternative materials such as sand-bentonite mixture and alumina red mud stabilized with gypsum were evaluated under field scale for the rehabilitation of calamina red muds and pyrite cinders respectively. Monitoring results showed that covering of the pyrite cinders with a sand-10% bentonite layer, 30 cm thick, reduced the volume of leachates by 72%. The reduction in the cumulative mass of metals dissolved was 90% for iron, copper and zinc, 83% for arsenic and 75% for lead. Regarding the calamina red mud, field tests indicated that alumina red mud addition reduced the amount of leachates produced by 50% (2% as compared to 4% of the total water added on the treated test pad and control respectively).

4.3 Chemical Stabilization of Metals in Oxidic Wastes and Soils

For Lavrion oxidic tailings, phosphates, fly ash and biological sludge, added to amounts 0.9, 8 and 10 % w/w, were proven to be efficient stabilisers reducing Pb and Cd leachability well below the regulatory limits. The most successful additives for Lavrion soils were phosphates, lime, red mud and fly ash at a dose of 1.4, 5, 5 and 7.5% w/w respectively. Alumina red mud stabilised with 5% gypsum was proven to be a successful stabilizing agent for Montevecchio soils.

Given that inorganic materials, e.g. phosphates, fly ash, lime, do not support plant growth, whereas the application of organic materials, e.g. biological sludge, peated lignite, has a beneficial effect on the production of biomass, the rehabilitation scheme currently tested under field scale involves mixtures of inorganic and organic materials including phosphates and peated lignite. The field test results indicated that treatment of soils and oxidic tailings with phosphates and peated lignite improved the leachates quality and plants growth and reduced metals uptake by plants.

4.4 Leaching Methods for the Clean-up of Contaminated Soils

The HCl-$CaCl_2$ process was selected as the most efficient treatment option for Montevecchio soils, due to their low calcite content, whereas the $Na_2CaEDTA$ process was considered as the best alternative for the calcareous soils of Lavrion. The results indicated that it is possible to achieve a high extraction of heavy metals, e.g., Pb 93-95%, Zn 78-85%, Cd 71-95% etc. The contaminants are recovered in a solid residue, corresponding to approximately 76 kg per ton soil on a dry basis. Finally, fresh water required for the final washing of treated soil was estimated to be approximately 1.6m^3 per ton soil.

5. COSTS

Available cost estimates of rehabilitation technologies examined are summarized in the following table:

Technology	Cost
Prevention	
Rehabilitation of acid-generating sulphidic wastes using alkaline additives (limestone and fly ash)	2-3 € / m^2
Immobilization of heavy metals in oxidic wastes and soils	22 € / m^3
Remedial	
Removal of heavy metals and toxic elements from soils by integrated leaching techniques (Chloride process)	30 € / ton
Removal of heavy metals and toxic elements from soils by integrated leaching techniques (EDTA process)	40 € / ton

6. REFERENCES

1. Cambridge, M. et al, 1995: "Design of a Tailing Liner and Cover to Mitigate Potential Acid Rock Drainage: A Geochemical Engineering Project" presented at the *1995 National Meeting of the American Society for Surface Mining and Reclamation*, Gillette, Wyoming.

2. Daniel, D.E., Koerner, R.M., 1993: Cover systems in geotechnical practice for waste disposal, ed. D.E. Daniel, Chapman and Hall, London, pp. 455-496.

3. Dessi R., R. Peretti, A. Xenidis, A. Zucca, I. Paspaliaris: Remediation of soil contaminated by heavy metals: batch and kinetic studies for Montevecchio soils, *SWEMP 2002*, Cagliari, Sardinia, 2002.

4. Elliot, H.A., Brown, G.A. & Shields, G.A., Lynn, J.H., 1989. Restoration of metal-polluted soils by EDTA extraction. In *Seventh International Conference on Heavy Metals in the Environment*, Geneva, vol.2, pp. 64-67.

5. Hessling, J.L., M.P. Esposito, R.P. Traver & R.H. Snow, 1989. Results of bench-scale research efforts to wash contaminated soils at battery recycling facilities. In J.W. Patterson & R. Passino (eds), *Metals Speciation, Separation and Recovery*, Chelsea Lewis Publishers Inc., vol.2, pp. 497-514.

6. Kontopoulos A., K. Komnitsas, A. Xenidis: Rehabilitation of the flotation tailings dam in Lavrion. Part II: Field application, *Clean Technologies for the Mining Industry*, M. A. Sanchez, F. Vegarra, S.H. Castro, ed., University of Concepcion, Chile 1996. pp. 391-400.

7. Krishnamurthy, S., 1992: Extraction and recovery of lead species from soil. *Environmental Progress*, vol. 11, pp. 256-260.

8. Leite, L. et al., 1989: Anomalous contents of heavy metals in soils and vegetation of a mine area in S.W. Sardinia, Italy. *Water, Air and Soil Pollution,* vol. 48, pp. 423-433.

9. Mylona E., A. Xenidis, I. Paspaliaris: Inhibition of acid generation from sulphidic wastes by addition of small amounts of limestone, *Minerals Engineering*, 13(10/11), 2000, pp.1161-1175.

10. Papassiopi, N., Tambouris, S., Skoufadis, C. and Kontopoulos, A., 1998: Integrated leaching processes for the removal of heavy metals from heavily contaminated soils, Contaminated Soil 98, Edinburg.

11. Peters, R.W. & L. Shem, 1992: Use of chelating agents for remediation of heavy metal contaminated soil. In ACS Symposium Series *Environmental Remediation*: 70-84.

12. Roche, E.G., J. Doyle & C.J. Haig, 1994: Decontamination of site of a secondary zinc smelter in Torrance California. In IMM, *Hydrometallurgy '94*: 1035-1048. London: Chapman & Hall

13. Royer, M.D., A. Selvakumar & R. Gaire, 1992: Control technologies for remediation of contaminated soil and waste deposits at superfund lead battery recycling sites. *J. Air & Waste Management Association*, pp. 970-980.

14. Shikatani, K.S., Yanful, E.K., 1993: An Investigation for the Design of Dry Covers for Mine Wastes, *in Proceedings of the International Symposium on Drying, Roasting, Calcining and Plant Design and Operation. Part II Advances in Environmental Protection for Metallurgical Industries*, eds: A. J. Olivier, W. J. Thornburn, R. Walli, 32nd Annual Conference of Metallurgists of CIM, Quebec, Aug. 29-Sep.2, pp. 245-258.

15. Stouraiti C., A. Xenidis, I. Paspailiaris: Use of lignite fly ash for chemical immobilisation of oxidic tailings and soils contaminated with heavy metals, *Water, Air and Soil Pollution*, 137(1), 2002, pp. 247-265.

16. Theodoratos P., A. Moirou, A. Xenidis, I. Paspaliaris: The use of municipal sewage sludge for the stabilisation of soil contaminated by mining activities, *Journal of Hazardous materials*, 77(1-3), 2000, pp.177-191.

17. Theodoratos P., N. Papassiopi and A. Xenidis: Evaluation of phosphates for the immobilization of lead in heavily contaminated soils from Lavrion, accepted for publication in *Journal of Hazardous Materials*, 2002.

18. Xenidis A., A. Moirou, P. Theodoratos, I. Paspaliaris: Design, construction and monitoring of the field tests for the stabilization of contaminated land, *Proceedings of the Intern. Conf. on Ecological Protection of the Planet Earth I,* Xanthi, Greece (Tsihrintzis, V.A. and P. Tsalidis eds.), 5-8 June 2001, pp. 369-377.

19. Xenidis A., C. Stouraiti, A. Moirou: The effectiveness of municipal sewage sludge application on the stabilization of Pb, Zn and Cd in a soil contaminated from mining activities, *Environmental Science and Health, Part A-Toxic/Hazardous Substances & Environmental Engineering*, 36(6), 2001, pp. 971-986.

20. Xenidis A., C. Stouraiti, I. Paspaliaris: "Stabilisation of oxidic tailings and solis by addition of calcium oxyphosphates: the case of Montevecchio site (Sardinia, Italy), *Journal of Soil Contamination*, 8(6), 1999, pp. 681-697.

21. Xenidis A., C. Stouraiti, I. Paspaliaris: Stabilisation of highly polluted soils and tailings using phosphates", in *Global Symposium on Recycling, Waste Treatment and Clean Technology, REWAS '99*, I. Gaballah, J. Hager, R. Solozabal, eds., San Sebastian, Spain, 1999, pp. 2153-2162.

22. Xenidis A., E. Mylona, I. Paspaliaris, K. Theodoridis: Application of lignite fly ash for the remediation of pyrite concentrates, *Proceedings of the Intern. Conf. on Ecological Protection of the Planet Earth I,* Xanthi, Greece (Tsihrintzis, V.A. and P. Tsalidis eds.), 5-8 June 2001, pp. 357-367.

23. Xenidis A., E. Mylona, I. Paspaliaris: Potential use of lignite fly ash for the prevention of acid generation from sulphidic wastes, *Waste Management*, 22(6), 2002, pp. 631-641.

24. Xenidis A., K. Komnitsas, S. Tabouris, A. Kontopoulos: Use of alkaline additives and a soil cover for prevention of acid mine drainage from sulphidic tailings, *Mining Environmental Management,* 8(6), 2000, pp. 14-18.

Project No. 5 **Application of Bioscreens and Bioreactive Zones**			
Location Rademarkt (former dry cleaning site) Rotterdam Harbour (oil refinery site) Rural Area (natural gas production site) Akzo Nobel (chlorinated pesticides site)	**Project Status** Final report	**Contaminants** Oil, BTEX, chlorinated solvents, chlorinated pesticides, and benzenes	**Technology Type** *In situ* bioremediation
Technical Contact Herco Van Liere/Huub Rijnaarts/Sjef Staps TNO Institute of Environmental Sciences, Energy Research and Process Innovation Laan van Westenenk 501 7334 DT Apeldoorn The Netherlands Tel: +31 55 5493380 Fax: +31 55 5493410 E-mail: H.H.M.Rijnaarts@mep.tno.nl S.Staps@mep.tno.nl	**Project Dates** Accepted 1998 **Costs Documented?** Yes	**Media** Groundwater **Project Size** Pilot to full-scale	**Results Available?** Yes

Project 5 was completed in 2000.

1. INTRODUCTION

Name of the technology: Biowalls/Bioscreens/Biobarrier/Treatment zones

Status of the technology: bench, pilot to full scale; emerging and innovative

Project objectives: To develop and demonstrate the technical and economical feasibility of various biowall/bioscreen configurations for interception of mobile groundwater contaminants, as a more cost-effective and groundwater resources saving alternative for currently used pump-and-treat approaches.

2. SITE DESCRIPTIONS

Chlorinated solvent site. The Rademarkt Site (Groningen, The Netherlands) is contaminated with perchloroethylene (PCE) and trichlorethylene (TCE). It concerns an unconfined aquifer with a clay aquitard at a depth of 9 m. The plume is located at a depth of 6 - 9 m and 150 m long and 30 to 60 m wide, and has mixed redox conditions, i.e. separate reducing and oxidising zones. Transformation rates of especially vinylchloride as observed in the field (and in the laboratory) are too slow to prevent migration of this hazardous compound to areas to be protected. Source remediation and plume interception are therefore required.

Oil refinery site. At this site in the Rotterdam Harbour area, it is required to manage a plume of the dissolved fraction of a mineral oil/gasoline contamination (80% of the compounds belong to the C6 - C12 fraction).

Aromatic hydrocarbon (BTEX) sites. At three sites in the north part of the Netherlands, deep anaerobic aquifers contaminated with Benzene, Toluene, Ethylbenzene or Xylenes (BTEX) have been investigated. Under the existing sulfate-reducing conditions, the intrinsic biodegradation of toluene and ethylbenzene could be demonstrated in the field and in microcosm studies. Benzene was shown to be persistent. Managing the benzene plumes, i.e. by enhanced in-situ bioprocesses, is therefore required.

Chlorinated pesticides site. Hexachlorocyclohexane (HCH) isomers are important pollutants introduced by the production of lindane (gamma HCH). Natural degradation of all HCH-isomers was demonstrated at the site of investigation. Interception of the HCH/Chlorobenzene/benzene plume is needed to protect a canal located at the boundary of the site.

3. DESCRIPTION OF PROCESS

Chlorinated solvent site. Laboratory experiments identified that a mixture of electron-donors is most suitable to enhance the in situ reductive dechlorination. In situ full-scale demonstration of enhanced anaerobic degradation in the source zone designed for complete reductive dechlorination is currently performed. The same technology is considered to be applied later at the head of the plume in terms of a treatment zone.

Oil refinery site. Bench scale experiments have been finished and established: i) optimal grain-size and packing density for the porous media used in the trench, ii) optimal oxygen supply rates to sufficiently initiate aliphatic hydrocarbon biodegradation and to minimise clogging with iron (III) oxides. Three different technologies are being tested at pilot scale: two gravel filled reactive trenches with biosparging units and one biosparging fence, without excavation of the soil. Each pilot application has a length of 40 m, and a depth of 4 meters.

Aromatic hydrocarbon (BTEX) sites. Microcosms were used to investigate possibilities to stimulate biodegradation of benzene and TEX compounds. Especially, addition of nitrate and low amounts of oxygen to the anaerobic systems appears to be the appropriate way to create down-stream biostimulated zones. Pilot demonstration tests are currently performed. One pilot test is a biostimulated zone with dimensions of 10 to 10 meters.

Chlorinated pesticide site. A bioactivated zone as an alternative to conventional large-scale pump-and-treat is currently being investigated. Laboratory process research indicated that a combination of anaerobic-microaerophilic in-situ stimulation in a bioactivated zone is the most feasible approach. Preparations are being made to incorporate the installation of the biotreatment zone in new building activities ate the site.

4. RESULTS AND EVALUATION

The status of most projects is that they recently have entered a pilot or a full-scale phase. First evaluations of technology performance are to be expected at the end of 1999.

5. COSTS

In a separate cost-analyses project, the costs of investment and operation of various bioscreen configurations (i.e. the funnel-and-gate^{TM}, the reactive trench and the biostimulated zone configuration) is being evaluated for various sites. The results indicate that biotreatment zones are in most cases the cheapest and most flexible approach, whereas funnel-and-gate^{TM} systems and reactive trenches have a cost level comparable to conventional pump-and-treat. Biotreatment zones have therefore the greatest market perspective, whereas funnel-and-gate^{TM} systems and reactive trenches can be used when a high degree of protection is required or when these approaches can be integrated with other building activities planned at the site.

6. REFERENCES AND BIBLIOGRAPHY

1. Bosma, T. N. P., Van Aalst, M.A., Rijnaarts, H.H.M., Taat, J., & Bovendeur, J. (1997) Intrinsic dechlorination of 1,2-dichloroethane at an industrial site monitoring of extensive in-situ biotechnological remediation. In: *In Situ and On Site Bioremediation, the 4th International Symposium*, New Orleans, Louisiana, April 28-May 1.

2. Brunia, A., Van Aalst-van Leeuwen, M.A., Bosma, T.N.P., & Rijnaarts, H.H.M. (1997) Feasibility study on the *in situ* bioremediation of chlorinated solvents using in situ electrochemical generation of hydrogen (In Dutch) Internal TNO-report.

3. De Kreuk, H., Bosma, T.N.P., Schraa, G., & Middeldorp, P. (1998) Complete in situ biodegradation of perchloroethylene and trichloroethylene under anaerobic conditions. CUR-NOBIS, Gouda, The Netherlands, Nobis report, project no 95-2-19

4. Gerritse, J., Alphenaar, A., & Gottschal, J.C. (1998) Ecophysiology and application of dechlorination anaerobes. ASCE Conference on Environmental Engineering, 6-10 June, Chicago.

5. Gerritse, J., Borger, A., van Heiningen, E., Rijnaarts, H.H.M., Bosma, T.N.P. 1999, in press. Presented at the In situ and on-site Bioremediation, the fifth international symposium, San Diego, USA, April 19-22, 1999.

6. Gerritse, J., Schraa, G., & Stams, F. (1999). Dechlorination by anaerobic microorganisms. 9th European Congress of Biotechnology (ECB9), July 11-15, Brussels.

7. Griffioen, J., Rijnaarts, H.H.M., van Heiningen, E., Hanstveit, B., & Hiddink, H. (1998) Benzene degradation under strongly reducing conditions (In Dutch, with English summary) CUR-NOBIS, Gouda, The Netherlands. Nobis project no. 96-3-05 (in press)

8. Koene, J. J. A., Rijnaarts, H.H.M. 1996. In-situ activated bioscreens: a feasibility study (in Dutch, with English summary) R 96/072. TNO-MEP.

9. Langenhoff, A. A. M., van Liere, H.C., Harkes, M.H., Pijls, C.G.J.M., Schraa, G., Rijnaarts, H.H.M. 1999, in press. Combined Intrinsic and Stimulated In Situ Biodegradation of Hexachlorocyclohexane (HCH). Presented at the In situ and on-site Bioremediation, the fifth international symposium, San Diego, USA, April 19-22, 1999.

10. Nipshagen, A., Veltkamp, A. G., Beuming, G., Koster, L.W., Buijs, C.E.H.M., Griffioen, J., Kersten, R.H.B., & Rijnaarts, H.H.M. (1997). Anaerobic degradation of BTEX at the sites Slochteren and Schoonebeek 107, (In Dutch, with English abstract). CUR-NOBIS, Gouda, The Netherlands, Nobis report project no. 95-1-43.

11. Rijnaarts, H. H. M. (1997). Data requirements for in-situ remediation. NICOLE-workshop "Site assessment & characterisation", TNO-MEP, Apeldoorn, 22-23 January.

12. Rijnaarts, H. H. M. & Sinke, A. (1997). Development and acceptance of guidelines for safe application of natural attenuation. NICOLE-workshop, Compiegne/France, 17-18 April.

13. Rijnaarts, H. H. M., Brunia, A., & Van Aalst, M.A. (1997). In-situ bioscreens. *In: In situ and on-site bioremediation, the 4th International Symposium*, New Orleans, Louisiana, April 28 - May 1.

14. Rijnaarts, H. H. M., De Best, J.H., Van Liere, H.C., & Bosma, T.N.P. (1998) Intrinsic biodegradation of chlorinated solvents: from thermodynamics to field. Nobis/TNO report. CUR-NOBIS, Gouda, The Netherlands, NOBIS project no. 96004

15. Rijnaarts, H. H. M., Van Aalst-van Leeuwen, M.A., Van Heiningen, E., Van Buijsen, H., Sinke, A., Van Liere, H.C., Harkes, M., Baartmans, R., Bosma, T.N.P., & Doddema, H.J. (1998b). Intrinsic and enhanced bioremediation in aquifers contaminated with chlorinated and aromatic hydrocarbons in the Netherlands. 6th International FZK/TNO Conference on Contaminated soil, Edinburgh, 17-21 May.

16. Rijnaarts, H.H.M. (1998) Application of biowalls/bioscreens. NATO-CCMS Pilot Project on Contaminated Land and Groundwater (Phase III), annual report no. 228, EPA/542/R-98/002, p. 19 - 20.

17. Rijnaarts, H.H.M. (1998) Bioprocesses in treatment walls. NATO-CCMS Pilot Study on Contaminated Land and Groundwater (Phase III), Special session Treatment walls and Permeable Reactive Barriers, report no. 229, EPA/542/R-98/003, p. 44 - 47.

18. Schippers, B. P. A., Bosma, T.N.P., Van den Berg, J.H., Te Stroet, C.B.M., Van Liere, H.C., Schipper, L., & Praamstra, T.F. (1998) Intrinsic bioremediation and bioscreens at dry cleaning sites contaminated with chlorinated solvents. (In Dutch, with English abstract). CUR-NOBIS, Gouda, The Netherlands, NOBIS-report project no. 96-2-01

19. Van Aalst-van Leeuwen, M. A., Brinkman, J., Keuning, S., Nipshagen, A.A.M., & Rijnaarts, H.H.M. (1997) Degradation of perchloroethene and trichloroethene under sequential redox conditions Phase 1, partial results 2-6: Field characterisation and laboratory studies. (In Dutch, with English abstract) CUR-NOBIS, Gouda, The Netherlands, Nobis report project no. 95-1-41

20. Van Eekert, M.H.A., Staps J.J.M., Monincx J.F., Rijnaarts H.H.M. (1999) Bitterfeld: Bioremediation of contaminated aquifers. Partial report 1 of the TNO-NOBIS participation in the SAFIRA project, Bitterfeld, Germany. TNO-MEP Apeldoorn, The Netherlands, Report no. TNO-MEP-R99/106, pp 43.

21. van Heiningen, E., Nipshagen, A.A.M., Griffioen, J., Veltkamp, A.G., Rijnaarts, H.H.M. 1999, in press. Intrinsic and enhanced Biodegradation of Benzene in strongly reduced aquifers. Presented at the In situ and on-site Bioremediation, The fifth international symposium, San Diego, april 19-22, 1999.

22. Van Liere, H. C., Van Aalst-van Leeuwen, M.A., Pijls, C.G.J.M., Van Eekert, M.H.A., & Rijnaarts, H.H.M. (1998) In situ biodegradation of hexachlorocyclohexane (HCH). 5th International HCH and Pesticides Forum IHOBE, 25-27 June 1998, LEIOA.

Project No. 6

Rehabilitation of a Site Contaminated by PAH Using Bio-Slurry Technique

Location	**Project Status**	**Contaminants**	**Technology Type**
Former railroad unloading area, Northern Sweden	Interim	Coal tars, phenols, cyanides, metals, ammonium compounds	Ex situ bioremediation
Technical Contact	**Project Dates**	**Media**	
Erik Backlund Eko Tec AB Näsuddsvägen 1o 93221 Skelleftehamn Sweden Tel: +46/910-33366 Fax: +46/910-33375 E-mail: erik.backlund@ebox.tninet.se	Accepted 1996 Final Report 2001	Soil	
	Costs Documented?	**Project Size**	**Results Available?**
	No	Full-scale (3,000 tons)	Yes

Information in this project summary is current as of May 1998.

1. INTRODUCTION

Eko Tec AB is a Swedish environmental engineering company dealing with problems posed by hazardous wastes, soil, and water pollution. Main clients are the oil industry, Swedish National Oil Stockpile Agency, and the Swedish State Railways.

In 1995, Eko Tec was contracted for bioslurry remediation of approximately 3,000 tons of creosote-contaminated soil and ditch sediments from a railway station area in the northern part of Sweden. A clean-up criterion of 50 ppm total-PAH was decided by the environmental authorities. For the specific PAH compounds benzo(a)pyrene and benzo(a)anthracene, a cleanup criterion of 10 ppm was decided.

Full-scale treatment has been preceded by bench- and pilot-scale treatability studies carried out at the Eko Tec treatment plant in Skelleftehamn, Sweden.

2. SITE DESCRIPTION

Not available

3. DESCRIPTION OF THE PROCESS

3.1 Pretreatment

The contaminated soil was initially treated to reduce volume. Stones and boulders were separated from the rest of the soil. In the next step, the soil was screened in a 10 mm sieve. Soil with a grain size less than 10 mm was mixed with water and later pumped to wet-screening equipment, in which particles >2 mm were separated from the process. The remaining soil fraction (<2 mm) was pumped to a 60 m3 slurry-phase bioreactor for further treatment. The volume of the treated soil fraction (<10 mm) was approximately 25 m^3. Samples were taken from the soil before water was added.

3.2 Slurry-Phase Bioreactor Treatment

Slurry-phase treatment was carried out in a 60 m^3 Biodyn reactor. During treatment, the soil/water mixture was continuously kept in suspension. In order to optimize the degradation rate, an enrichment culture containing microorganisms that feed on PAH was added to the slurry, together with nutrients and soil activators. During the treatment phase, dissolved oxygen, nutrient concentration, temperature, and pH were monitored continuously.

After 27 days of treatment, the cleanup criteria were met and the slurry-phase treatment process was closed. The slurry was pumped to a concrete basin where the treated soil was separated from the water by sedimentation. The waster was stored for reuse in the text treatment batch. The treated soil will be reused as fill material.

3.3 Monitoring Program

In order to determine the initial PAH concentration, a soil sample was taken from the soil fraction <10 mm. During the wet screening process, a soil sample was taken from the separated soil (<2 mm fraction). Samples were also taken from the slurry phase during treatment. Soil samples were stored by freezing, and then sent to the laboratory. The same accredited laboratory was used during the project period.

4. RESULTS

Cleanup criteria were met in 14 days. The initial PAH concentration (total PAH) was 219.9 ppm. Final concentration after 27 days of treatment was 26.97 ppm, which is well below the cleanup criterion of 50 ppm. PAH compounds benzo(a)pyrene and benzo(a)anthracene were occurring in concentrations below the cleanup criterion of 10 ppm.

5. COSTS

Not yet available.

Project No. 7

Risk Assessment for a Diesel-Fuel Contaminated Aquifer Based on Mass Flow Analysis During Site Remediation

Location Menziken/Studen, Switzerland	**Project Status** Final	**Media** Groundwater	**Technology Type** In situ bioremediation
Technical Contact Mathias Schluep Frohburgstrasse 184 8057 Zurich Switzerland Tel: +41-79-540-5557 mathias@schluep.ch Christoph Munz BMG Engineering Ltd Ifangstrasse 11 8057 Schlieren Switzerland Tel: +41-1-732-9277 Fax: +41-1-730-6622 E-mail: christoph.munz@bmgeng.ch Josef Zeyer Soil Biology Inst. of Terrestrial Ecology ETHZ Grabenstrasse 3 8952 Schlieren Switzerland Tel: +41-1-633-6044 Fax: +41-1-633-1122 E-mail: zeyer@ito.umw.ethz.ch	**Project Dates** Accepted 1997 Final Report 2000	**Contaminants** Petroleum hydrocarbons (diesel fuel, heating oil)	
	Costs Documented? No	**Project Size**	**Results Available?** Yes

Project 7 was completed in 2000.

1. INTRODUCTION

The studies were aimed to give a scientific basis for an evaluation procedure, allowing us to predict the treatability of a petroleum hydrocarbon (PHC) contaminated site with in situ bioremediation technologies [1]. This includes the description of the risk development with time and the quantification of the remediation efficiency by identifying critical mass flows. The focus of the project was set on the modeling of movement and fate of compounds typically found in non-aqueous phase liquids (NAPLs) such as PHCs in the subsurface.

2. SITE DESCRIPTION

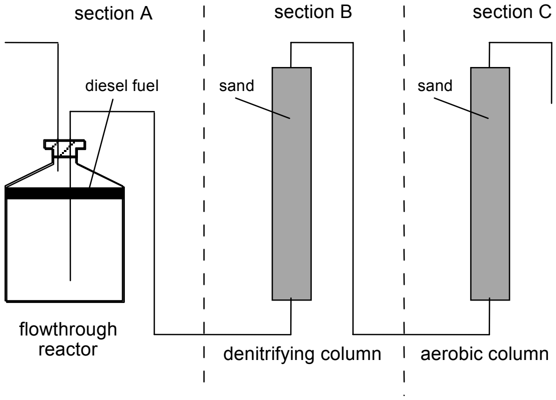
At the *Menziken site* [2] the contaminated aquifer was remediated based on the stimulation of indigenous microbial populations by supplying oxidants and nutrients (biorestoration). Detailed investigations were made from 1988 until 1995. The engineered in situ bioremediation took place from 1991 - 1995.

At the *Studen site* [3] no engineered remedial actions were taken. The investigations started in 1993 and led to a better understanding of the biological processes occurring in the aquifer. It could be shown that intrinsic bioremediation is a major process in the removal of PHC at this site.

3. DESCRIPTION OF THE RESEARCH ACTIVITY

PHC contain benzene, toluene, ethylbenzene, and xylenes (BTEX) and polycyclic aromatic hydrocarbons (PAH), which are regulated hazardous compounds. These substances potentially dissolve into groundwater in relevant concentrations at petroleum release sites, posing risks to drinking water supplies. Understanding this process is important, because it provides the basis to perform initial remedial actions and plan a long term remedial strategy for contaminated sites. Fortunately the dissolved BTEX and PAH compounds are degradable under various conditions in aquifers. The biodegradation process leads to a reduction of total mass of PHCs. Therefore the evaluation of the effectiveness of the biodegradation processes is another key step in applying in situ remediation techniques to reduce risks. These processes were studied in a laboratory system consisting of the following sequence (Figure1): dissolution of PHCs into the aqueous phase (section A), anaerobic (section B) and aerobic biodegradation (section C) of the dissolved compounds.

Figure 1: Experimental setup of the laboratory study on dissolution of diesel fuel compounds into sterile groundwater (section A) and biodegradation in two laboratory aquifer columns under denitrifying (section B) and aerobic (section C) conditions



4. RESULTS AND EVALUATION

4.1 Dissolution of NAPL Compounds in a Batch System

The purpose of the first study was to develop a modeling approach for the quantification of mechanisms affecting the dissolution of NAPLs in the aqueous phase using the slow stirring method (SSM) and thus to provide a tool for the interpretation of experimental data regarding the interaction between NAPLs and water [4]. Generally, mass transfer from the NAPL to the aqueous phase increases with the stirring rate. This can be interpreted as a decrease of the thickness of the aqueous stagnant layer at the water/NAPL interface across which diffusion occurs. Therefore, the time to reach saturation depends on the mechanical agitation and the aqueous diffusion coefficient of the chemical. This is only true as long as transport within the NAPL does not control the overall mass transfer of the different NAPL components. It is known that NAPL viscosity can influence the dissolution kinetics of PAHs. The phenomenon was attributed to transport limitation within the NAPL of constituents with high viscosity. Thus, the existence of a depletion zone in the NAPL phase (which in the SSM is not directly stirred) was postulated.
An analytical model was developed to provide a qualitative understanding for the different processes that determine the temporal evolution of the combined NAPL/aqueous phase system. For situations were the employed quantitative approximations are no longer valid a short recipe how the equations can be solved numerically and without restrictions regarding the relative size of certain terms was presented. The theoretical framework was validated with experimental data. The experiment was performed by running section A of the laboratory setup (Figure 8) in batch mode.

With focus on the applicability of the preparation of water soluble fractions in slow stirring batch system the results can be summarized as follows: Once equilibrium is reached in the system a fraction of a compound will be transferred from the NAPL phase into the aqueous phase leading to a lower concentration in the NAPL phase. Equilibrium concentrations in the aqueous phase therefore will be lower compared to calculations based on initial concentrations in the NAPL phase. This effect is only relevant for relatively soluble substances like benzene and in the presence of small NAPL volumes and is independent of the NAPLs viscosity. The relative diffusivities of the NAPL compounds govern the dissolution kinetics in terms of mass transfer limitations within the NAPL phase. Thus, in low viscosity NAPLs, the depletion process is controlled by diffusion within the NAPL layer of relatively soluble substances like benzene, whereas in high viscosity NAPLs, even the dissolution of relatively insoluble substances like Naphthalene may be diffusion-limited. With the theoretical framework presented the mechanisms affecting the dissolution of NAPLs into the aqueous phase in slow stirring batch systems can be quantified. The models allow us to predict the errors in equilibrium concentrations and the time frame to reach saturation.

4.2 Dissolution of NAPL Compounds in a Flow Through System

The objective of the second study was twofold: First the dynamic changes of NAPL-water equilibria as the soluble compounds deplete from a complex NAPL mixture was studied. Second an easy to use model based on Raoult’s law to predict such dissolution patterns with respect to time varying NAPL mass and composition was developed [5].

The experimental setup consisted of a flow through vessel containing deionized water and diesel fuel. The resulting concentrations in the water were measured in the effluent of the vessel. The results were compared with the calculated aqueous concentrations based on Raoult's law for supercooled liquid solubilities. The model considers the dynamic changes of the diesel fuel / water equilibrium due to continuous depletion of the soluble compounds from diesel fuel.

It could be shown that Raoult's law is valid during dynamic dissolution of aromatic compounds from complex NAPL mixtures (e.g., diesel fuel) in non-disperse liquid/liquid systems (in this case the SSM). This is true as long as a significant depletion of substances is observable. At low concentrations in the NAPL phase non-equilibrium effects probably play a major role in the dissolution behavior, resulting in underestimation of the aqueous concentration. However deviations at these concentration levels are not important from a risk point of view. The quality of predictions was improved by considering time varying NAPL mass. Although the model could be confirmed in an idealized laboratory system, it can not be applied to complex field situations with the same accuracy. However this study provides a simple method to assess contaminated sites on an "initial action" basis and supports the planning of long term remedial strategies at such sites.

4.3 Biodegradation of Dissolved NAPL Compounds

The effluent of the flow through vessel was fed into two columns filled with quartz sand which were operated in series [6]. The first column was operated under enhanced denitrifying conditions whereas the second column was operated under aerobic conditions (Figure1, section B and C). The two columns represent two degradation zones downstream of a contamination plume under different redox conditions as it is commonly found in contaminated aquifers. As an example of the measured BTEX and PAH compounds observed benzene and ethylbenzene concentration curves in the effluent of the flow through reactor (section A), the denitrifying column (section B) and the aerobic column (section C) respectively are drawn in Figure 2. Degradation under denitrifying conditions only occurred in the case of ethylbenzene, whereas benzene seems to be persistent to denitrification. The slight decrease of benzene concentrations in the effluent of the denitrifying column is attributed to small amounts of oxygen intruded into the system at the beginning of the experiment. Under aerobic conditions benzene and ethylbenzene were rapidly degraded. Based on these results a mass balance was performed for each compound as well as for the total amount of diesel constituents after each section of the experimental setup (Figure1) and compared with the depletion of the electron acceptor. Results indicate that the fate of toxicologically relevant compounds is predictable by measuring inorganic compounds.

The development of risk with time was calculated after each section of the experiment (Figure1) using the corresponding concentrations of the relevant compounds as well as their toxicological properties. The non-carcinogenic risk (Figure3) as well as the carcinogenic risk (data not shown) is dominated by benzene, which is depleted from the NAPL rapidly. Since benzene is not readily degraded under anaerobic conditions the risk is not significantly reduced under these conditions. However, after the introduction of oxygen as it occurs in the field due to groundwater mixing, the risk is instantly reduced to acceptable levels.

Figure 2: Benzene and ethylbenzene concentration curves in the effluent of the flow through reactor (section A), the denitrifying column (section B) and the aerobic column (section C) respectively of the continuous flow-through experiment.

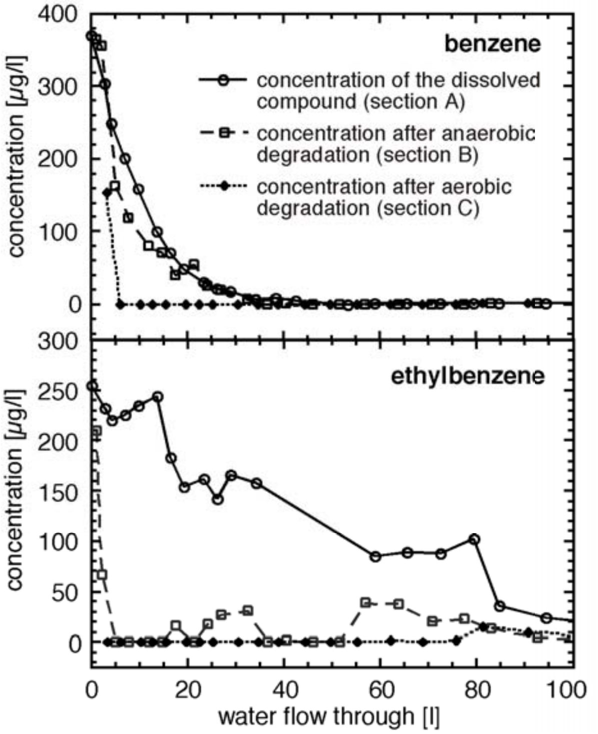
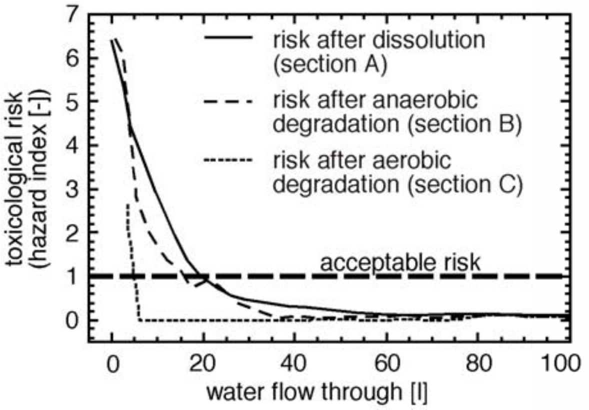


Figure 3: Development of the toxicological risk (hazard index) after the dissolution of single compounds from diesel fuel into the aqueous phase and after anaerobic and aerobic degradation respectively. The hazard index was calculated as the additive risk of the single BTEX and PAH compounds.



4.4 Correlation with Field Data

Results from the laboratory studies including the mathematical models finally were applied at the field sites in Studen and Menziken in order to perform a risk assessment [7-9]. Several assumptions to simplify the complex field situation and to acquire unknown parameters had to be made. This lead to the following findings:

Using the composition data of diesel fuel or heating oil, the maximal concentrations of toxicologically relevant compounds expected in the groundwater can be predicted (worst case scenario).
The efficiency of in situ bioremediation techniques can be assessed. With a mass balance calculation of the inorganic species (oxygen, nitrate, etc.) measured in the Studen groundwater it could be determined that about 200 kg of PHC were biodegraded within the time frame of 5 years. Comparing this result with a theoretical calculation based on the mathematical dissolution model it could be shown that the removal of 200 kg PHC through the dissolution process alone would take about 50 years. This indicates that biological processes enhance the depletion of PHC, and hence shorten the time for PHC removal from the subsurface.

Based on mass flows the duration of a site-remediation can be estimated at the level of single compounds. Modeling the dissolution and biodegradation processes of the heating oil spill in Studen, we can predict that aqueous benzene concentrations drop below detection limit and therefore is expected to be depleted from the NAPL phase after 3 years, ethylbenzene after 30 years, and naphthalene after 130 years. These results correlate well with concentrations measured in groundwater samples of the five years old spill. The impact of the remediation process on the risk development can be predicted. The risk in Studen and Menziken was calculated to have been above acceptable levels during the first two years after the spill happened. As soon as the more soluble compounds such as benzene are dissolved completely the risk drops below unacceptable levels. At "older" hazardous sites involving diesel fuel or heating oil spills, the risk therefore may be already significantly reduced.

5. CONCLUSIONS

The remediation of PHC contaminated sites usually occurs naturally without engineered remediation activities mainly through the biodegradation of compounds dissolved in the groundwater. Since every site has its own geochemical and biological characteristic the decision whether additional actions have to be taken in order to reduce risks for human and the environment has to be made on a site-by-site basis. Using simple tools such as mass balances and distribution models the applicability and efficiency of in situ bioremediation technologies at PHC spill sites can be assessed.

6. REFERENCES AND BIBLIOGRAPHY

1. Schluep M. 2000. Dissolution, biodegradation and risk in a diesel fuel contaminated aquifer — modeling and laboratory studies. Dissertation No. 13713, Swiss Federal Institute of Technology ETH, Zurich, Switzerland.

2. Hunkeler D, Hoehener P, Bernasconi S, Zeyer J. 1999. Engineered in situ bioremediation of a petroleum hydrocarbon contaminated aquifer: Assessment of mineralization based on alkalinity, inorganic carbon and stable isotope balances. J Contam Hydrol 37:201-223.

3. Bolliger C, Hoehener P, Hunkeler D, Haeberli K, Zeyer J. 1999. Intrinsic bioremediation of a petroleum hydrocarbon contaminated aquifer and assessment of mineralization based on stable carbon isotopes. Biodegradation 10:201-217.

4. Schluep M, Imboden DM, Gaelli R, Zeyer J. 2000. Mechanisms affecting the dissolution of non-aqueous phase liquids into the aqueous phase in slow stirring batch systems. Environ Tox Chem, 20(3).

5. Schluep M, Gaelli R, Imboden DM, Zeyer J. 2000. Dynamic equilibrium dissolution of complex non-aqueous phase liquid mixtures into the aqueous phase, in preparation.

6. Schluep M, Häner A, Gälli R, Zeyer J. 2000. Bioremediation of petroleum hydrocarbon contaminated aquifers: laboratory studies to assess risk development, in preparation.

7. Kreikenbaum S, Scerpella D. 1999. Risikobewertung eines Heizoelschadenfalls. Diplomarbeit Eidgenoessische Technische Hochschule ETH, Zurich, Switzerland.

8. Schluep M, Gälli G, Munz C. 1999. Mineralölschadenfälle - wie weiter. TerraTech 6:45-48

9. Wyrsch B, Zulauf C. 1998. Risikobewertung eines mit Dieselöl kontaminierten Standortes. Diplomarbeit Eidgenoessische Technische Hochschule ETH, Zurich, Switzerland.

Project No. 8

Obstruction of Expansion of a Heavy Metal/Radionuclide Plume Around a Contaminated Site by Means of Natural Barriers Composed of Sorbent Layers

Location	**Project Status**	**Contaminants**	**Technology Type**
Istanbul University	Interim Report	Heavy metals (Pb, Cu, Cd) and radionuclides (137Cs, 90Sr, 238U), textile dyes	In situ adsorption and stabilization/ solidification
Technical Contact	**Project Dates**	**Media**	
Resat Apak Istanbul University Avcilar Campus, Avcilar 34850 Istanbul, Turkey Tel: 90/212-591-1996 Fax: 90/212-591-1997 E-mail: rapak@istanbul.edu.tr	Accepted 1998 Final Report 1999	Soil and groundwater (unconventional sorbents e.g., red muds and fly ashes, simulate hydrous oxide-like soil minerals; kaolinite and feldspar represent clay minerals)	
	Costs Documented?	**Project Size**	**Results Available?**
	No	Bench-scale	Partly

Project 8 was completed in 1999.

1. INTRODUCTION

When a spill or leakage of a heavy metal/radionuclide contaminant occurs, in situ soil and groundwater technologies are generally preferred to cope with the contaminants and to prevent their dispersion outside the site. Barrier wall technologies employ immediate action that restricts the expansion of the contaminant plume. Thus, this project involves a laboratory-scale investigation of the use of metallurgical solid wastes and clay minerals as barrier materials to adsorb toxic heavy metals and radionuclides from water (a fixation or stabilization process) followed by solidification of the metal-loaded mass in a cement-based block totally resistant to atmospheric weathering and leaching conditions.

2. BACKGROUND

Metals account for much of the contamination found at hazardous waste sites. They are present in the soil and groundwater (at approximately 65% of U.S. Superfund sites) coming from various metal processing industrial effluents. Turkey also has metal (Pb, Cd, Cu, Cr, U, etc.) contaminated sites due to effluents predominantly from battery, electroplating, metal finishing, and leather tanning industries, and mining operations.

Cesium-137 and strontium-90, with half-lives of 30 and 28 years, respectively, pose significant threats to the environment as a result of fallout mainly from power plant accidents. In Turkey, 137Cs became a matter of public concern after the Chernobyl accident, especially contaminating the tea plant harvested in the Black Sea Coast of the country. On the other hand, milk products and other biological materials containing Ca were extensively investigated for possible 90Sr contamination. Land burial of low-level radioactive wastes also poses a contamination risk to groundwater.

Physical/chemical treatment processes specific to metals/radionuclides include chemical precipitation, ion exchange, electrokinetic technologies, soil washing, sludge leaching, membrane processes, and common adsorption. When adsorption is employed, there is an increasing trend toward substitution of pure adsorbents (e.g., activated carbon, alumina, and other hydrated oxides) with natural by-products, soil minerals or stabilized solid waste materials (e.g., bauxite waste red muds and fly ashes). These substances also serve as barrier material for passive wall technologies utilized around a heavy metal spill site or shallow-land burial facility of low-level radioactive wastes. Once these contaminants are stabilized within barrier walls, it is also desirable to fix them in an environmentally safe form by performing in situ stabilization/solidification by way of adding cement—and pozzolans if necessary—to obtain a durable concrete mass. The host matrix for metals and radionuclides, i.e., red muds, fly ashes, and clay minerals, may serve as inexpensive pozzolanic binders to be used along with cement for solidification.

The aim of this Pilot Study project is to develop unconventional cost-effective sorbents for basically irreversible fixation of heavy metals/radionuclides; these sorbents should show high capacities and fast retention kinetics for the so-called contaminants. The determination of conditions affecting stabilization/solidification of the loaded sorbents by adding pozzolans and cement is also aimed. Durability and leachability of the final concrete blocks have to be tested. Modeling of sorption of heavy metals/radionuclides onto the tested materials has to be made in order to extend the gained knowledge to unforeseen cases. Finally a reasonable unification of in situ physical/chemical treatment technologies applicable to a spill/leakage site will be accomplished.

3. TECHNICAL CONCEPT

The effect of various parameters (sorbent grain size, pH, time of contact, contaminant concentration, metal speciation, etc.) affecting the adsorption/desorption behavior of the selected heavy metals onto/from the sorbents has been investigated. The sorption capacity (batchwise and dynamic column capacities) and leachability of the sorbents in terms of heavy metals/radionuclides have been estimated by the aid of batch contact, column elution and standard leaching (simulating groundwater conditions) tests. Possible interferents (e.g., inert electrolytes as neutral salts) have been incorporated in the synthetic contaminant solutions so as to observe any incomplete adsorption or migration of contaminants that may occur under actual field conditions. The sorption data have been analyzed and fitted to linearized adsorption isotherms. New mathematical models have been developed to interpret equilibrium adsorption data with simple polynomial equations.

Red muds and fly ashes, after being loaded to saturation with Pb(II), Cd(II) and Cu(II), were solidified to concrete blocks that should not pose a risk to the environment. The setting and hardening characteristics of mortars, as well as the flexural and mechanical strengths of the solidified specimens, were optimized with respect to the dosage of natural and metal-loaded solid wastes. Extended metal leaching tests were carried out on the solidified samples.

These treatment steps actually serve the perspective of unification of seemingly separate physical/chemical technologies for the removal of heavy metals/radionuclides in environmentally safe forms. The developed barrier materials in a way resemble iron hydroxides and oxyhydroxides that are currently developed from low-cost iron waste streams by DuPont (Hapka, 1995). In the meantime, although not directly fitting with the project title, the usage of iron fillings as potential barrier material has been tested for the management of textile dyeing wastes, e.g., as a restricting agent for an uncontrolled expanding plume from a permeable storage lagoon or pond where textile wastes are collected.

4. ANALYTICAL APPROACH

The metallurgical solid wastes used as sorbents were supplied from Turkish aluminium and thermal (coal-fired) power plants, and characterized by both wet chemical and X-ray (diffraction and fluorescence) analysis. They were subjected to chemical treatment (water and acid washing) for stabilization, and classified with respect to size when necessary. Their surface areas were determined by BET/N_2 surface area analysis, and their surface acidity constants (pK_a) by potentiometric titration.

After equilibrating the sorbents with the metal solutions, all metal determinations in the centrifugates were made with flame atomic absorption spectrometry (AAS) using a Varian SpectrAA FS-220 instrument. The beta activities of the Cs-137 and Sr-90 radioisotope containing centrifugates were counted by an ERD Mullard Geiger Muller tube type MX 123 system with halogen extinction. The batch and dynamic adsorption and desorption tests were carried out in thermostatic shakers and standard Pyrex glass columns, respectively.

A mortar-mixing mechanical apparatus, ASTM Vicat apparatus, steel specimen moulds (4x4x16 cm^3), tamping-vibrating apparatus, and testing equipment for flexural and compressive strength tests were used for following the solidification process and the mechanical strength of the final concrete blocks.

The textile dyes used for modeling textile wastes were analyzed by UV/visible spectrophotometry.

The adsorption isotherms conforming to Langmuir, Freundlich, B.E.T. and Frumkin isotherm equations were evaluated by linear regression and non-linear curve fitting of experimental data.

5. RESULTS

The distribution coefficients of metals (as log K_D) between the solid (red mud, fly ash, etc.) and solution phases varied between 1-3 and showed a gradual decrease with increasing equilibrium concentration of the metal remaining in solution.

The Langmuir saturation capacities of the sorbents (in the units of mg metal per g sorbent as red mud-fly ash, in this order) for the metals averaged at approximately 50-200 mg Cd.g–1, 40-100 mg Cu.g–1, and 100-350 mg Pb.g–1.

The adsorption isotherms were somewhat S-shaped B.E.T. type isotherms showing layered sorption at the natural pH of equilibration, but saturation of the sorbent was attained at a definite concentration enabling an approximated Langmuir evaluation of equilibrium data in operational sense.

The order of hydrolysable divalent metal cation retention on the selected sorbents was as follows in terms of molar saturation capacities: Cu > Pb > Cd for fly ashes and Cu > Cd > Pb for red muds. The degree of insolubility of the metal hydroxides approximately followed the same order. The simulation of CO_2-injected groundwater conditions were achieved by saturated aqueous CO_2 (pH 4.8) and carbonic acid/bicarbonate buffer (pH 7.0) solutions. The heavy metals (Cu, Pb, Cd) retained on the sorbents were not leached out by these carbonated leachant solutions.

Heavy metal adsorption onto red muds, either as free metal ion or in chelated metal-EDTA forms, has been effectively modeled for (M+M-EDTA) mixtures. The adsorption data could be theoretically generated by using simple quadratic equations in terms of covalently- and ionically- adsorbed metal concentrations in the sorbent phase, once the total metal concentration prior to equilibration and final solution pH were known.

As for solidification of the metal-loaded solid wastes, when these loaded wastes were added up to 20% by mass to Portland cement-based formulations, the fixed metals did not leach out from the solidified concrete blocks over extended periods, with the exception of Cu(II), which reached a concentration of 0.4 ppm after 8 months in a water leachate of pH 8-9. 2% setting accelerator $Ca3(PO_4)^{2-}$added improved formulations could bear only 10% of lead-loaded fly ash, while this tolerance could be raised to 20% fly ash by incorporating (3% $Ca_3(PO_4)_2$+1% $CaCl_2$) mixed additive.

The studied radionuclides did not show a significant temperature dependency in adsorption. Especially radiostrontium retention increased with pH. These observations are in accord with ion exchange mechanism of sorption. Radiocesium adsorption is maximal around neutral pH, which is specific for most natural waters.

Of the textile dyes tested, acid blue and acid yellow showed 75-90% and 60-80% removal, respectively, when passed through a granular iron bed at an initial concentration of 10-100 ppm dye containing 0.10 M HCl in solution.

6. HEALTH AND SAFETY

The primary components of the unconventional sorbent suspensions, i.e., red muds and fly ashes containing Fe_2O_3, Al_2O_3, SiO_2, TiO_2, and some aluminosilicates, to be used as barrier material are essentially non-toxic. The tested heavy metals, either as free ions or in chelated forms, i.e., Cd^{2+}, Pb^{2+} (and partly Cu^{2+}) and Cd-$EDTA^{2-}$, Pb-$EDTA^{2-}$, Cu-$EDTA^{2-}$, were toxic, so care should be exercised especially in solidification/ stabilization processes using the heavy metal-loaded sorbents in dry form, where small particles could be inhaled by workers. Also working with radionuclide solutions, even in very dilute forms, needs special pipettes and glassware to be used under a hood on a stainless steel workbench, and special laboratory practice with workers wearing radiation dosimeters. All waste solutions, even at very low-level activity, should be properly collected and submitted to the nuclear energy authority for waste storage and stabilization.

7. ENVIRONMENTAL IMPACTS

Prior acid or water leaching of the sorbents before adsorption experiments did not effectively increase the specific surface area or chemical adsorption power of these sorbents, but rather these sorbents were stabilized so as not to leach out any micropollutants to water at the time of heavy metal adsorption. It is also indicated in literature that iron oxyhydroxide based grouts as barrier material can be made from low cost industrial by-products, which should be tested for safety and effectiveness on a case-by-case basis (Hapka et al., 1995). Thus these criteria should be judged for red muds and fly ashes.

Stabilization/solidification of the metal-loaded solid wastes puts these wastes and incorporated toxic metals into environmentally safe (mechanically strong, durable and unleachable) forms. The matrix disrupting effect of Pb was eliminated by using relatively small amounts of sodium aluminate or calcium phosphate to improve the setting, hardening and mechanical properties of the final concrete blocks. It was environmentally safe to observe that the matrix-held metals (either as a result of irreversible adsorption or solidification) did not leach out by carbonate or carbonic acid solutions ensuring the chemical stability of these solid wastes under changing groundwater conditions.

8. COSTS

Because iron-based grouts (without relatively expensive additives such as citric acid, urea, and urease) can be prepared from inexpensive by-products, the primary costs involved come from transportation and additives (Jet grouted, 25% grout) roughly around 50 USD per m^2 for 1m thick wall, i.e., or 50 USD for 1 cubic meter. The overall cost data have not yet been obtained.

9. CONCLUSIONS

In investigation of the possibility of usage of metallurgical solid wastes as cost-effective sorbents in heavy metal (Pb, Cu, Cd) and radionuclide (Cs-137 and Sr-90) removal from contaminated water, red muds and especially fly ashes have been shown to exhibit a high capacity. Extensive modeling of heavy metal sorption—either as free metal ions or in the form of EDTA-chelates—has been performed by simple quadratic equations in terms of the retained metal concentration in the sorbent phase. These modeling efforts enable the prediction of heavy metal adsorption in different media over a wide pH and concentration range. The developed iron- and aluminum-oxide based sorbents may be used as barrier material as cost-effective grout for the prevention of expansion of a heavy metal contaminant plume.

Heavy metal-loaded solid wastes have been effectively solidified by adding cement, sand, and water. The setting and mechanical properties of concrete specimens obtained by optimal dosage of waste addition were satisfactory. The fixed heavy metals did not leach out appreciably into water over extended periods.

The usage of iron fillings as potential barrier material has been successfully tested for the management of textile dyeing wastes, i.e., acid blue and acid yellow.

A unified passive technological process for the in situ sorption of heavy metals, radionuclides, and textile wastes using iron oxide-, alumina- and silica-based metallurgical solid wastes functioning as barrier material in conjunction with granular metallic iron is on the way of development. The presumed process is planned to be finished with in situ stabilization/solidification.

10. REFERENCES

1. S. Arayici, R. Apak and V. Apak, "Equilibrium modeling of pH in environmental treatment processes," J. Environ. Sci. and Health, Pt. A-Environ. Sci. and Eng., 31 (1996) 1127-1134.

2. R. Apak, G. Atun, K. Güçlü, E. Tütem and G. Keskin, "Sorptive removal of cesium-137 and strontium-90 from water by unconventional sorbents. I. Usage of bauxite wastes (red muds)," J. Nucl. Sci. Technol., 32 (1995) 1008-1017.

3. R. Apak, G. Atun, K. Güçlü and E. Tütem, "Sorptive removal of cesium-137 and strontium-90 from water by unconventional sorbents. II. Usage of coal fly ash," J. Nucl. Sci. Technol., 33 (1996) 396-402.

4. F. Kilinçkale, S. Ayhan and R. Apak, "Solidification-stabilization of heavy metal-loaded red muds and fly ashes," J. Chem. Technol. Biotechnol., 69 (1997) 240-246.

5. R. Apak, E. Tütem, M. Hügül and J. Hizal, "Heavy metal cation adsorption onto unconventional sorbents (red muds and fly ashes)," Water Research, 32 (1998) 430-440.

6. R. Apak, "Heavy metal and pesticide removal from contaminated groundwater by the use of metallurgical waste sorbents," NATO/CCMS International Meeting, 18-22 November 1991, Washington, DC, USA.

7. R. Apak, "Uranium (VI) adsorption by soil in relation to speciation," Mediterranean Conference on Environmental Geotechnology, 24-27 May 1992, Çesme, Turkey.

8. E. Tütem and R. Apak, "The role of metal-ligand complexation equilibria in the retention and mobilization of heavy metals in soil," Contaminated Soil'95 Proceeding of the Fifth International FZK/TNO Conference on Contaminated Soil, 30 Oct.-3 Nov. 1995, Maastricht, Netherlands, W. J. van den Brink, R. Bosman and F. Arendt (eds.), Kluwer Academic Publishers, Vol. I, 425-426.

9. R. Apak, "Sorption/solidification of selected heavy metals and radionuclides from water," NATO/CCMS Pilot Study International Meeting on 'Evaluation of Emerging and Demonstrated Technologies for the Treatment of Contaminated Land and Groundwater', 17-21 March 1997, Golden Colorado, USA.

10. K. Güçlü, unpublished Ph.D. thesis (Supervisor: R. Apak), "Investigation and modeling of heavy metal adsorption dependent upon pH and complexing agents," Department of Chemistry, Faculty of Engineering, Istanbul University, 1999, Istanbul.

11. M. Hapka, J. S. Thompson and J. M. Whang, "Method for precipitating a solid phase of metal," 1995, provisional patent application.

12. R. R. Rumer and J. K. Mitchell, "Assessment of barrier containment technologies," International Containment Technology Workshop, 29-31 Aug. 1995, Baltimore, Maryland: Proceedings, pp. 221-223.

13. K. Güçlü and R. Apak, "Investigation of adsorption of free- and bound- EDTA onto red muds for modeling the uptake of metal-organic complexes by hydrated oxides," 19th International Meeting on Organic Geochemistry, 6-10 Sept. 1999, Istanbul (accepted as presentation).

<table>
<tr><td colspan="4">Project No. 9
Solidification/ Stabilization of Hazardous Wastes</td></tr>
<tr><td>Location
Middle East Technical University, Ankara, Turkey</td><td>Project Status
Final Report</td><td>Contaminants
PCBs, AOX (adsorbable organic halides), heavy metals</td><td>Technology Type
Solidification/ Stabilization</td></tr>
<tr><td rowspan="2">Technical Contact
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E-mail: kunlu@metu.edu.tr</td><td>Project Dates
Accepted 1998
Final Report 2001</td><td colspan="2">Media
Soil, mining waste and wastewater and sludge from pulp and paper industry</td></tr>
<tr><td>Costs Documented?
No</td><td>Project Size
Bench Scale</td><td>Results Available?
Yes</td></tr>
</table>

Project 9 was completed in 2001.

1. INTRODUCTION

Solidification and stabilization are treatment processes designed to either improve waste handling and physical characteristics, decrease surface area across which pollutants can transfer or leach, or limit the solubility or to detoxify the hazardous constituents (EPA, 1982). They also refer to techniques that attempt to prevent migration of contaminated material into the environment by forming a solid mass.

Although solidification and stabilization are two terms used together, they have different meanings. Solidification refers to techniques that encapsulate the waste in a monolithic solid of integrity. The encapsulation may be of fine waste particles (microencapsulation) or of a large block or container of wastes (macroencapsulation). Solidification does not necessarily involve a chemical interaction between the wastes and the solidifying reagents, but may mechanically bind the waste into the monolith. Contaminant migration is restricted by vastly decreasing the surface area exposed to leaching and/or by isolating the wastes within an impervious capsule. Stabilization refers to techniques that reduce the hazard potential of a waste by converting the contaminants into their least soluble, mobile, or toxic form. The physical nature and handling characteristics of the waste are not necessarily changed by stabilization (Conner and Hoeffner, 1998).In practice, many commercial systems and applications involve a combination of stabilization and solidification processes. Solidification follows stabilization to reduce exposure of the stabilized material to the environment through, for example, formation of a monolithic mass of low permeability (Smith, 1998). This project focuses on investigating the effectiveness of solidification/stabilization (S/S) technology by conducting bench scale treatability tests with contaminated soils and various types of hazardous waste materials. The major objectives of the project are *(i)* to investigate the effectiveness and reliability of the S/S technology for the safe disposal of hazardous wastes containing metal and organic contaminants, and *(ii)* to determine the appropriate technical criteria for applications based on the type and composition of hazardous wastes

2. BACKGROUND

With the enforcement of the *Hazardous Wastes Control Regulation* in August 1995, the direct or indirect release of hazardous wastes into the receiving environment in such a manner that can be harmful to human health and the environment is banned in Turkey. The main purpose of the regulation is to provide a legal and technical framework for the management of hazardous wastes throughout the nation. In this regard, the regulation is applicable not only to hazardous wastes to be generated in the future, but also concerns with the existing hazardous wastes and their safe disposal in compliance with the current regulation. The S/S technology is recognized by the *Turkish Hazardous Wastes Control Regulation* (THWCR) as a promising new emerging technology for the safe disposal of hazardous wastes. This recognition by the regulation plays a major role for the initiation of this project.

3. TECHNICAL CONCEPT

The following technical criteria is considered for the evaluation of the effectiveness of the S/S technology for the safe disposal of hazardous wastes containing metal and organic contaminants: *(i)* determining the mobility of contaminants in the waste via conducting leaching and permeability tests on solidified/stabilized samples; and *(ii)* determining the strength of solidified samples against deformation and deterioration via conducting unconfined compressive strength tests on solidified samples.

In this study, for metals a residue material from gold mining, for organics PCB contaminated soil and AOX containing sludge and wastewater from pulp and paper industry were used. Although mining waste has relatively high heavy metal content, use of mining waste with very high metal content was considered to serve better for the purpose of assessing the performance of S/S technology. Concentrated mining waste was obtained by the addition of heavy metal salts of chromium nitrate, cadmium nitrate, lead nitrate, copper sulfate and zinc sulfate. Water content of wastewater sludge was initially very high; thus it was dried in an oven at 60^{o}C to remove water and then ground into powder before S/S process. Initial analysis of the PCB-contaminated soil showed that it did not contain significant quantities of PCBs. T7herefore, transformer oil containing PCBs was added to the soil at the rate of 5 ml of oil to 100 grams of soil, which yielded oil concentration of 43000 ppm in the soil. Particle size distribution of the soil was approximately 33% silt, 60% sand and 7% gravel and soil was classified as “silty-sand”.

For solidification of waste and encapsulation of contaminants, portland cement as a binding agent was mixed with waste materials at different ratios. This ratio was determined based on particle size distribution of waste materials. In general, as the fraction of fine particles in the waste increases the amount of portland cement to be used decreases. On the other hand, as the fraction of coarse particles in the waste increases, the strength of solidified waste against deformation increases at the same ratio of portland cement and waste material mixture. Waste material and portland cement mixing ratios were determined considering these general facts. For mining residue, two samples representing fine, and coarse particle size distribution were prepared. In order to prepare the coarse particle size distribution, sand was added to the waste. The mixing ratio of sand to waste + cement + moisture was 1:1. For each waste material representing a given particle size distribution class, two different portland cement mixing ratio was used. The objectives were to determine the effects of binding agent ratio and particle size distribution of waste material on S/S process and the metal retention efficiency of portland cement as a binding agent. Mixing ratios for different waste groups are given in Table1.

Table 1: Waste material and portland cement mixing ratios

Waste Material	Cement Addition (% by weight)
Waste material from gold mining (fine texture)	10 and 20 %
Waste material from gold mining (coarse texture)	10 and 20 %
Wastewater from pulp and paper industry	83 and 88 %
Sludge from treatment of pulp and paper industry wastewater	30 and 50 %
PCB-contaminated soil	20 and 35 %

4. ANALYTICAL APPROACH

Prior to S/S process, physical and rheological characteristics of waste materials were determined. For mining waste and PCB-contaminated soil, maximum dry density, optimum moisture content, Atterberg limits, specific gravity and particle size distribution were determined. For AOX containing sludge, only maximum dry density and optimum moisture content were determined. Particle size distributions of mining waste and PCB-contaminated soil were determined using hydrometer and sieving methods, respectively. Standard Proctor Compaction Test was performed to determine maximum dry density and optimum moisture content. In order to test ability of solidified/stabilized waste samples to withstand overburden loads, unconfined compressive strength tests were performed on samples using Compression Test Equipment. Hydraulic conductivity of solidified/stabilized waste samples was measured using a flexible wall permeameter under a hydraulic gradient of 113.

All waste and cement mixtures were prepared by adding optimum moisture content and then compacted to corresponding maximum dry density in cylindrical molds having a height of 71 mm and a diameter of 36 mm. After compaction, cylindrical samples were removed from the molds and placed in a 95 % humidity room for 28 day-curing. At the end of the 28-day cure period, duplicate samples of solidified/stabilized waste were used for strength and hydraulic conductivity tests. Prior to the performance of leaching tests, solidified samples were crushed and passed through sieves for fractionation to aggregate sizes between 1-2 mm and >2 mm. Then, duplicates of crashed waste samples from each aggregate size fraction were subjected to leaching test. Based on the physical tests and chemical compositions of leachate obtained from leaching tests, the effectiveness of S/S in terms of contaminant encapsulation was assessed for each waste type and cement ratio combination.

The level of effectiveness of S/S process in terms of reducing contaminant mobility is evaluated through hydraulic conductivity and leaching tests. In this study, as leaching test *Toxicity Characteristic Leaching Procedure* (TCLP) of the U.S. Environmental Protection Agency (U. S. EPA) and *Distilled Water Leaching Procedure* (DWLP) of THWCR were used. TCLP and DWLP were applied using 2 and 3 grams of duplicate waste samples from each aggregate size fraction, between 1-2 mm and >2 mm.

Prior S/S process, initial metal composition of mining waste and portland cement were determined by acid (HNO_3-HF) digestion method (Infante and Acosta, 1988). The leachate of solidified waste samples obtained from TCLP were analysed for various metals (Cr^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Ca^{2+}, Mg^{2+}, Na^+, and K^+) and anions (Cl^- ,SO_4, CO_3^{2-} and PO_4^{3-}) using standard methods (AWWA-APHA, 1989). For the analyses of metals, except for sodium and potassium, Flame Atomic Absorption Spectrophotometer was used; analyses of sodium and potassium were carried out by Flame Photometer. Sulfate and phosphate were measured by spectrophotometer. The measurement of sulfate was based on turbidimetric method. For the measurement of phosphate, ascorbic acid method was used. Chloride and carbonate analyses were based on titrimetric methods. AOX analyses were done based on German DIN-3849 method using Euroglas BV microcoulometer equipment. Measurement of PCB was based on microwave-assisted solvent extraction method 3546 and gas chromatography method 8080 of EPA SW-846.

5. RESULTS

5. 1 Mining Waste

A. Chemical Analyses for Waste-Cement Mixtures

Prior to 28-day cure period, initial metal composition of the mining waste was determined. Because portland cement, as binding agent, was mixed with waste material, metal composition of portland cement was also determined to see any contribution to the metal content of waste. The results of total metal compositions of mining waste material and portland cement are given in Table 2. As seen in the table, main constituents of portland cement used in this study were calcium, magnesium, aluminium and iron as expected. Initial total metal analyses of mining waste material showed that heavy metal (Cd, Cr, Cu, Pb, and Zn) concentrations were relatively high except for cadmium.

Table 2: Metal Compositions of Portland Cement and Mining Waste Material Before (Initial) and After (Final) Metal Salt Addition

Metals	Portland Cement (mg/kg)	Waste (Initial) (mg/kg)	Waste (Final) (mg/kg)
Cd	BDL[a]	40	970
Cu	30	2410	3640
Cr	500	350	2410
Pb	BDL	3480	4380
Zn	40	2380	3760
Fe	15630	29700	32210
Al	29070	30890	30090
Ca	276310	440	640
Mg	8240	1150	1570

[a]BDL: Below detection limit (for Cd, 0.05 mg/L)

Table 3 provides an overview of various cleanup goals based on total metal concentrations. If these values are exceeded, the soil or waste will be classified as “contaminated”. Therefore, initial total metal concentrations of mining waste should be much higher than these standards in order to be classified as hazardous. Upon comparing these cleanup values (Table 3) with Table 2, it can be seen that initial total metal concentrations of mining waste do not exceed cleanup goals much except for copper and lead. In order to assess the performance of S/S technology effectively, presence of much higher heavy metal concentrations in the mining waste may serve better for the purpose.

To increase metal concentration levels, solutions of nitrate or sulfate salts of five heavy metals (Cd, Cr, Cu, Pb, and Zn) were added to the mining waste. The added salts were chromium nitrate, cadmium nitrate, lead nitrate, copper sulfate and zinc sulfate. Final metal composition of mining waste material is given in Table 2. By the addition of metal salts, metal concentrations in the waste reached the desired high levels and original concentrations for each metal, except for Cr, increased approximately by 1000 mg/kg. The low Cr concentration may result form non-homogeneous mixing of the waste material and metal salts.

Table 3: Various Cleanup Goals for Total Metals

Total Metal Cleanup Goals	Cd (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Cu (mg/kg)	Zn (mg/kg)
Superfund Site Goals From Technical Resource Document	3 to 20	6.7 to 375	200 to 500	- [a]	- [a]
California Total Threshold Limit Concentration	100	500	1000	- [a]	- [a]
Louisiana Cleanup Standards For Contaminated Soil	20	100	100	1500	2800

[a] not specified among the goals

In addition to the initial metal compositions of mining waste material and portland cement, total metal analyses of samples of waste-cement mixtures at the end of 28-day cure period were performed. The purpose was to obtain the chemical composition of these waste samples before leaching tests. The results are given in Table 4. As seen from the table, metal concentrations of coarse waste samples were diluted due to addition of sand, which shifted the texture of waste from silt (fine) to sand (coarse). Moreover, since coarse waste mixed with 20% portland cement contained less original waste compared to the one mixed with 10% portland cement, total metal concentrations were the lowest in coarse textured waste containing 20% portland cement. All waste samples also have very high concentrations of Fe, Al, Ca and Mg due to high concentrations of these metals in the portland cement.

Table 4: Chemical composition of fine and coarse mining waste and cement mixtures

Metals (1)	10% cement Fine (mg/kg) (2)	10% cement Coarse (mg/kg) (3)	20% cement Fine (mg/kg) (4)	20% cement Coarse (mg/kg) (5)
Cd	1250	850	1000	750
Cu	3330	1690	2550	1250
Cr	3060	1920	2140	1770
Pb	3090	1420	2320	1210
Zn	1900	1350	1990	1050
Fe	13500	10470	13310	8780
Al	26130	11170	24360	8250
Ca	7830	15540	17720	19400
Mg	1710	3100	2490	1560
K	21550	9950	12950	9000
Na	27780	7150	20000	21000

B. Physical Analyses

Prior to S/S, some physical characteristics, such as Atterberg limits, maximum dry density, optimum moisture content, specific gravity and particle size distribution of mining waste and cement mixtures were determined. Among these, values of optimum moisture content and corresponding maximum dry density were used to determine for each case the volume of water to be added to waste-cement mixture and the mass at which waste-cement mixture to be compacted. Results are given in Table 5. As seen from the table, coarse textured waste-cement mixtures have higher dry densities and corresponding low optimum moisture contents. Soil classification of the samples in Table 5 was made based on their plasticity index and particle size distribution. Addition of sand to waste-cement mixture changed soil classification of fine waste samples from ML (silt-low plasticity) to SM (silty sands) and decreased liquid limit values of coarse waste-cement mixtures.

C. TCLP Leaching Tests

TCLP provides a measure of metal concentration that leach from the solid phase of a waste sample when extracted in an acetic acid solution. It is designed to simulate leaching conditions to which a waste disposed in a landfill may be exposed (Pritts et al., 1999). Therefore, one of the most important technical criteria for testing the effectiveness of S/S process is the quality of TCLP leachate. At the end of 28-day cure period, TCLP was applied and leachate obtained for each waste group (fine and coarse waste, 10% and 20% cement; crashed solidified sample aggregate size between 1-2 mm and > 2mm) was analyzed for heavy metals and some ions. The results of these analyses are given in Table 6. In general, at the same cement ratio, fine waste samples produced leachate having lower metal concentrations than coarse waste samples. Therefore, when initial waste characterization is taken into consideration, waste samples having finer textures will result in better S/S process. Despite slight difference between initial metal compositions of cement-waste mixtures, increasing cement ratio from 10% to 20% did not have any considerable effect on metal concentrations in the leachate of the same fine or coarse textured waste.

Table 5: Physical characteristics of fine and coarse mining waste and cement mixtures

Characteristics (1)	10% cement Fine (2)	20% cement Fine (3)	10% cement Coarse (4)	20% cement Coarse (5)
Dry density (gcm^{-3})	1.77	1.78	2	2
Optimum moisture content (%)	15	17	10	11
Liquid limit (%)	28	28	22	22
Plastic limit (%)	18	20	17	16
Plasticity index (%)	10	8	5	6
Soil classification	ML (silt-low plasticity)	ML(silt-low plasticity)	SM (silty sands)	SM(silty sands)
Specific gravity	2.72	2.73	2.67	2.75
Particle size distribution	18% clay 55% silt 27% sand	22% clay 52% silt 26% sand	12% clay 29% silt 59% sand	13% clay 29% silt 58% sand

Table 6: The chemical compositions of TCLP and DWLP leachates obtained from mining waste solidified at different cement ratios

Ions	10% cement, fine				20% cement, fine				10% cement, coarse				20% cement, coarse			
	1-2 mm		>2 mm		1-2 mm		>2 mm		1-2 mm		>2 mm		1-2 mm		>2 mm	
	TCLP mg/L	DWLP mg/L	TCLP mg/L	DWLP mg/L	TCLP mg/L	DWLP mg/L	TCLP mg/L	DWLP mg/L	TCLP mg/L	DWLP mg/L	TCLP mg/L	DWLP mg/L	TCLP mg/L	DWLP mg/L	TCLP mg/L	DWLP mg/L
Cd	1.85	0.23	3.89	ND	0.47	0.12	0.58	0.08	2.0	0.29	2.41	0.13	0.73	0.16	0.19	0.12
Cu	0.31	ND	0.44	ND	0.41	0.12	0.38	0.07	0.92	0.51	0.68	0.27	0.91	0.51	0.29	0.22
Cr	0.37	ND	ND	ND	0.59	0.55	0.58	0.59	1.71	0.60	0.76	0.19	2.22	1.03	0.95	0.68
Pb	0.39	ND	0.23	ND	0.58	0.45	0.48	0.39	1.12	0.51	0.76	0.35	1.38	0.55	0.22	0.13
Zn	0.71	0.24	1.85	0.31	0.5	0.07	0.35	0.02	0.96	0.33	1.04	0.15	0.77	0.24	0.17	0.05
Fe	ND	ND	ND	ND	1.94	0.84	1.09	0.51	3.69	3.08	2.2	0.70	2.35	2.18	0.78	0.62
Al	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ca	94.6	83.39	93.5	80.83	172.1	114.5	161.3	117.5	288	162.1	286.6	170.4	218.4	144.2	215.4	136.7
Mg	17	6.31	18.31	4.95	21.98	4.25	23.63	6.35	30.7	8.31	29.25	8.76	3.16	0.227	5.73	0.36
K	58	19	30.5	19	45.5	19	43	19	21.5	20	21.5	20	20	11.5	19.75	12.5
Na	152.2	36	385	28	760.7	7.7	773.7	6.45	266	10.35	260	8.4	995	19.3	1001	25.6
SO_4^{2-}	149.9	76.5	143.8	78.1	36.7	4.47	26.96	16.3	53.58	8.77	66.29	0	17.12	4.6	19.63	2.3
PO_4^{3-}	0.31	25.02	0.58	8.94	0.88	0	1.12	0	1.44	0	0	0	2.14	2.2	0.08	4.57
Cl^-	150	274.9	208.3	224.9	495.3	574.8	482.9	524.8	386.4	418.9	623.8	468.9	605.3	320.9	555.3	220.9
CO_3^{2-}	1854	4320	1320	1440	1110	2370	300	4020	2940	1350	1500	630	495	780	735	150

ND: Concentration is below the detection limit (for Cd, 0.05 mg/L; Cu, 0.05 mg/L; Cr 0.1 mg/L; Pb 0.1 mg/L; Fe, 0.5 mg/L and Al, 5 mg/L)

For metals, the U.S. EPA defines toxicity characteristic limits based on metal concentrations measured in the TCLP leachates (U. S. EPA, 1997). These toxicity characteristic limits, which are given in Table 7 for metals studied in this work, mean that wastes containing metal concentrations in their TCLP extract exceed the listed concentrations are considered to be *characteristically hazardous* and said to have the toxicity characteristic. When the results of TCLP in Table 6 were compared with EPA toxicity characteristic limits, given in Table 7, it is observed that only Cd concentrations in the leachates of fine and coarse waste samples mixed with 10% cement exceeded the regulated level. All the other metal concentrations in the leachate were much lower than these regulated levels. This higher Cd concentration in TCLP leachate of 10% cement-waste samples may be due to somewhat lower leachate pH, which was around 6, of 10% cement-waste samples. This slightly acidic leachate condition probably caused dissolution of Cd, for which lower pH limit to precipitate is 6.8 (Table 7), and thus prevented its precipitation within the cement matrix. Results of Cioffi *et al.* (1998) support this observation by stating that cadmium is retained within the matrix provided that pH does not drop to the acid range. Overall, from a regulatory perspective leachate quality indicates that S/S process is effective for all (fine and coarse textured wastes mixed with 10% and 20% cement) cases of the mining waste.

Table 7: The pH range for the quantitative precipitation and U.S. EPA toxicity characteristic limits of metals

Metals (1)	pH range for precipitation (2)	U.S. EPA toxicity characteristic limits (mg/L) (3)
Cd	6.8-12.0	1.0
Cr	5.4-10.0	5.0
Cu	5.4-12.0	130.0
Fe	2.3-12.0	30.0
Pb	6.0-9.0	5.0
Zn	5.3-9.0	500.0

For heavy metals, pH dependent precipitation reactions (i.e., hydroxides, carbonates, sulfates) are often an important stabilization mechanism. The pH of TCLP extraction fluid used for the mining waste was around 4.93, but after shaking fractionated solidified waste samples together with the extraction fluid, the final pH of TCLP leachates were within the range of 6.05 and 6.80. The pH of the extraction fluid, as expected, affected the final pH of leachates and also the alkalinity present in the cement leads to higher leachate pH values. Table 7 gives the pH range for the precipitation of heavy metals cadmium, chromium, lead, copper, iron, and zinc considered in this study (Porteus, 1985). At high pH, many metals reach their lowest solubility and precipitate as their respective insoluble hydroxides, carbonates, phosphates and etc. (LaGrega, 1994). Moreover, major aqueous components of cement such as Na^+, K^+, Ca^{2+}, Mg^{2+}, OH^- and SO_4^{2-} are potentially available ions to react with wastes and make insoluble precipitates of heavy metals (Glasser, 1997). Most of the metals in the mining waste are converted to insoluble precipitates during S/S process within the observed final pH range of TCLP leachates and are subsequently trapped within the pores of cement matrix.

With regard to aggregate size effect, results in Table 6 showed that crashing the solidified samples into aggregate size classes 1-2 mm and >2 mm did not affect the metal concentrations in the TCLP leachate. Increase in the leachate concentration with the decrease in the aggregate size was observed only for coarse waste sample with 20 % cement addition. Wiebusch *et al.* (1998) investigated much larger aggregate size classes (20-50 mm, 2-20 mm and <2 mm) obtained from solidified fly ash and found that leachate concentrations of heavy metals in samples with aggregate size <2 mm were 2.5 times greater than those in samples with aggregate size in the range of 20-50 mm.

Following TCLP extractions, percentages of metals retained in the solidified/stabilized mining waste were calculated to determine the amount of metals released into the leachate and in turn, to assess the effectiveness of S/S process. The following formula was used to calculate the retention efficiency, i.e., percent retention (% RT):

$$\%RT = \frac{M_T - (V_L)(C_L)}{M_T} x100$$

where M_T is the total initial mass of a given metal in the waste-cement mixture, *mg*; V_L is the volume of leachate, *L*; and C_L is the concentration of metal in the leachate, *mg/L*. For example, *%RT=90* means that 10% of the metal initially present in the waste-cement mixture transferred into the leachate while 90% of the metal still remained in the solidified waste. Thus, high values of *%RT* imply high degree effectiveness of S/S process. Values of *%RT* calculated for TCLP and DWLP are given in Table 8 and 9, respectively. According to these tables, S/S applications for all cases resulted in high degree of effectiveness. Although

Table 8: Percent retention efficiency of metal concentrations in S/S samples of mining waste after TCLP

Metals	10% cement, fine					20% cement, fine					10% cement, coarse					20% cement, coarse				
	C_i (mg/kg)	1-2 mm		>2 mm		C_i (mg/kg)	1-2 mm		>2 mm		C_i (mg/kg)	1-2 mm		>2 mm		C_i (mg/kg)	1-2 mm		>2 mm	
		C_l (mg/l)	RT (%)	C_l (mg/)	RT (%)		C_l (mg/l)	RT (%)	C_l (mg/l)	RT (%)		C_l (mg/l)	RT (%)	C_l (mg/l)	RT (%)		C_l (mg/l)	RT (%)	C_l (mg/l)	RT (%)
Cd	1250	1.85	97.0	3.89	93.8	1000	0.47	99.1	0.58	98.8	850	2	95.3	2.41	94.3	750	0.73	98.1	0.19	99.5
Cu	3330	0.31	99.8	0.44	99.7	2550	0.41	99.7	0.38	99.7	1690	0.92	98.9	0.68	99.2	1250	0.91	98.5	0.29	99.5
Cr	3060	0.37	99.8	ND	99.9	2140	0.59	99.4	0.58	99.5	1920	1.71	98.2	0.76	99.2	1770	2.22	97.5	0.95	98.9
Pb	3090	0.39	99.7	0.23	99.9	2320	0.58	99.5	0.48	99.6	1420	1.12	98.4	0.76	98.9	1210	1.38	97.7	0.22	99.6
Zn	1900	0.71	99.3	1.85	98.1	1990	0.5	99.5	0.35	99.6	1350	0.96	98.6	1.04	98.5	1050	0.77	98.5	0.17	99.7
Fe	13500	0.50	99.9	0.50	99.9	13310	1.94	99.7	1.09	99.8	10470	3.69	99.3	2.2	99.6	8780	2.35	99.5	0.78	99.8
Al	26130	5.0	99.6	5.0	99.6	24360	5.0	99.6	5.0	99.6	11170	5.0	99.1	5.0	99.1	8250	5.0	98.8	5.0	98.8
Ca	7830	94.6	75.8	93.5	76.1	17720	172.1	80.6	161.3	81.8	15540	288	62.9	286.6	63.1	19400	218.4	77.5	215.4	77.8
Mg	1710	17	80.1	18.31	78.6	2490	21.98	82.3	23.63	81.0	3100	30.7	80.2	29.25	81.1	1560	3.16	95.9	5.73	92.7

C_i: initial metal concentration in the waste
C_l: leachate concentration of metal
RT: percent retained metal concentration

Table 9: Percent retention efficiency of metal concentrations in S/S samples of mining waste after DWLP

Metals	10% cement, fine					20% cement, fine					10% cement, coarse					20% cement, coarse				
	C_i (mg/kg)	1-2 mm		>2 mm		C_i (mg/kg)	1-2 mm		>2 mm		C_i (mg/kg)	1-2 mm		>2 mm		C_i (mg/kg)	1-2 mm		>2 mm	
		C_l (mg/l)	RT (%)	C_l (mg/l)	RT (%)		C_l (mg/l)	RT (%)	C_l (mg/l)	RT (%)		C_l (mg/l)	RT (%)	C_l (mg/l)	RT (%)		C_l (mg/l)	RT (%)	C_l (mg/l)	RT (%)
Cd	1250	0.23	99.8	0.05	99.96	1000	0.12	99.9	0.08	99.9	850	0.29	99.7	0.13	99.8	750	0.16	99.8	0.12	99.8
Cu	3330	0.05	99.98	0.05	99.98	2550	0.12	99.95	0.07	99.97	1690	0.51	99.7	0.27	99.8	1250	0.51	99.6	0.22	99.8
Cr	3060	0.1	99.97	0.1	99.97	2140	0.55	99.7	0.59	99.7	1920	0.6	99.7	0.19	99.9	1770	1.03	98.4	0.68	99.6
Pb	3090	0.1	99.97	0.1	99.97	2320	0.45	99.8	0.39	99.8	1420	0.51	99.6	0.35	99.8	1210	0.55	99.5	0.13	99.9
Zn	1900	0.24	99.9	0.31	99.8	1990	0.07	99.96	0.02	99.99	1350	0.33	99.8	0.15	99.9	1050	0.24	99.8	0.05	99.95
Fe	13500	0.5	99.96	0.5	99.96	13310	0.84	99.94	0.51	99.96	10470	3.08	99.7	0.7	99.9	8780	2.18	99.8	0.62	99.9
Al	26130	5	99.96	5	99.8	24360	5	99.8	5	99.8	11170	5	99.6	5	99.6	8250	5	99.4	5	99.4
Ca	7830	83.39	89.4	80.83	89.7	17720	114.5	93.5	117.5	93.4	15540	162.1	89.6	170.4	89.0	19400	144.2	92.6	136.7	93.0
Mg	1710	6.31	96.3	4.95	97.1	2490	4.25	98.3	6.35	74.5	3100	8.31	97.3	8.76	97.2	1560	0.227	99.9	0.36	99.8

C_i: initial metal concentration in the waste
C_l: leachate concentration of metal
RT: percent retained metal concentration

fine waste samples mixed with 10% cement had initially the highest metal concentrations among the others, the effectiveness of S/S was also high for this case. In general, the finer the waste texture and higher the cement ratio, the higher the value of *%RT* and greater the effectiveness of S/S process. Despite very high *%RT* values (>94%) for all metals, Cd concentration in TCLP leachate of 10% cement-waste mixture exceeded the U. S. EPA regulatory limit when initial Cd concentration in the waste is high (> 850 mg/kg).

D. Unconfined Compressive Strength and Hydraulic Conductivity Tests

In addition to leaching tests conducted to determine the amount of contaminant that can be leached from the solidified wastes, the effectiveness of S/S process can also be assessed by testing the unconfined compressive strength and hydraulic conductivity of solidified/stabilized samples (Porteous, 1985). These tests have been adopted in order to evaluate the physical integrity and engineering properties of solidified and stabilized product in actual field conditions (Lagrega *et al*., 1994). Unconfined compressive strength and hydraulic conductivity tests were performed on duplicate cylindrical solidified samples of each treatment at the end of 28 days-cure period. These results are given in Table 10.

Table 10: Unconfined compressive strength (q_u) and hydraulic conductivity (K) values for mining waste samples solidified at different cement ratios

Property (1)	10% Cement, Fine (2)	20% Cement, Fine (3)	10% Cement, Coarse (4)	20% Cement, Coarse (5)
q_u, kPa	1153.46	2520.4	1019	3250
K, m/s	2.1×10^{-9}	1.09×10^{-9}	1.84×10^{-9}	1.04×10^{-9}

Solidified and stabilized wastes must have adequate strength to be able to support the loads of materials placed over them. In general for any given S/S agent, the stronger the solidified waste, the more effective S/S process (LaGrega *et al*., 1994). In this study, results of both fine and coarse textured wastes showed that unconfined compressive strength also increases with increasing cement ratio in the waste. The U.S. EPA defines a minimum unconfined compressive strength value of 350 kPa for the disposal of solidified hazardous wastes in landfills (U. S. EPA, 1992). Unconfined compressive strength values measured for all treatments considered in this study are well above this limiting value. Therefore, these solidified samples can easily be disposed of in landfills.

Solidified fine and coarse waste materials at the same cement ratio had similar hydraulic conductivity values. As the cement ratio increased hydraulic conductivity values decreased both for fine and coarse textured waste samples. As shown in Table 10, hydraulic conductivity values measured for all treatments were in the order of 10^{-9} m/s although higher cement addition (20%) results in somewhat lower conductivity values. Measured conductivity values are two orders of magnitude lower than the value of 10^{-7} m/s recommended by U.S. EPA for land-burial of stabilized wastes (U. S. EPA, 1989). Therefore, in terms of hydraulic conductivity criterion, mining waste can be disposed of in a landfill.

5.2 AOX Containing Pulp and Paper Wastewater and Sludge

For S/S of AOX containing sludge from pulp and paper industry, the same procedure was followed as in the case of mining waste. Since the samples were compacted into cylindrical molds at their optimum moisture content yielding maximum dry density, in terms of initial physical characterization, only optimum moisture content and corresponding maximum dry density values were measured. The results for sludge mixed with 30% and 50% portland cement are given in Table 11, which show a slight increase in the optimum moisture content of sludge samples with increasing portland cement addition and in turn, an increase in the corresponding dry density.

Table 11: Optimum moisture content and maximum dry density values for AOX-containing pulp and paper sludge

Material (1)	Optimum moisture content (%) (2)	Maximum dry density (g/cm^3) (3)
30% Cement-Sludge	18	1.27
50% Cement-Sludge	19	1.32

A. AOX Analyses

Prior to S/S of samples, initial AOX concentrations of wastewater and sludge were measured as39 mg/L and 400 mg/kg, respectively. Following the 28 day-S/S cure period, TCLP were applied to the solidified samples crashed to aggregate sizes between 1-2 mm and >2 mm. The results of AOX analyses in TCLP and DWLP leachates are given in Table 12 and 13 for wastewater and sludge, respectively. Results show that the cement-mixing ratio and aggregate size of the crashed solidified samples did not have any considerable effect on the AOX concentration in the leachate. AOX concentrations in the leachate decreased slightly with increase in the cement addition. Based on TCLP and DWLP results, AOX retention efficiency for solidified wastewater and sludge samples were determined as 90% and 85%, respectively.

Table 12: AOX concentrations in TCLP and DWLP leachates of wastewater solidified at different cement ratios

Wastewater: Cement Ratio	AOX Concentration (mg/L)			
	1-2 mm		> 2mm	
	TCLP	Water	TCLP	Water
1:6	3.24	3.22	3.35	3.30
1:8	3.20	3.19	3.33	3.14

Table 13: AOX concentrations in TCLP and DWLP leachates of pulp and paper sludge solidified at different cement ratios

% Cement added to sludge	AOX Concentration (mg/L)			
	1-2 mm		> 2mm	
	TCLP	Water	TCLP	Water
30%	3.37	3.43	3.22	3.45
50%	3.11	3.21	3.20	3.01

Unlike U. S. EPA, Turkish Hazardous Waste Control Regulation defines a specific hazardous waste criteria range of 0.6 to 3 mg/L for AOX in the leachate. If AOX concentration of a waste is within this range, then that waste is considered to be hazardous waste and need to be disposed of in a hazardous waste landfill without any pre-treatment before landfilling. But, if AOX concentrations exceed the upper limit, then waste should be treated before landfilling. Although application of S/S process to AOX containing sludge yielded high retention efficiency, concentrations of AOX in the TCLP leachates were above the regulated levels. That is, wastes having similar AOX concentrations as of these sludges do not seem to be disposed of directly in landfills.

B. Unconfined Compressive Strength and Hydraulic Conductivity Tests

At the end of the 28-day cure period, hydraulic conductivity and unconfined compressive strength tests were performed on duplicates of solidified/stabilized sludge samples. The results of these tests, which are given in Table 14, indicate that as expected, increase in the cement ratio increased the strength of solidified/stabilized samples. Unconfined compressive strength values measured for both 30% and 50%

cement cases are well above U. S. EPA limiting value of 350 kPa for the disposal of solidified hazardous wastes in landfills.

Table 14: Unconfined compressive strength (q_u) and hydraulic conductivity (K) values for AOX-containing pulp and paper sludge samples solidified different cement ratios

Property (1)	30% Cement (2)	50% Cement (3)
q_u, kPa	2990	3605
K, m/s	2.6×10^{-9}	1.8×10^{-9}

There was a decrease in hydraulic conductivity with higher cement addition. When the measured conductivity values were compared with the value of 10^{-7} m/s recommended by U.S. EPA for land-burial of stabilized wastes (EPA, 1989), measured values were two orders of magnitude lower than the recommended value of EPA. Therefore, in terms of hydraulic conductivity criterion, these samples can be disposed of in landfills.

5.3 PCB-Contaminated Soil

A. Physical Analyses

Prior to S/S of PCB-contaminated soil, Atterberg limits and particle size distribution of soil were determined. In addition, optimum moisture content and corresponding maximum dry densities of soil-cement mixtures were determined. Results are presented in Table 15. Although there was no change in the optimum moisture content, maximum dry density increased with high cement addition. Atterberg limits of the contaminated soil showed that the soil is non-plastic. Based on particle size distribution analysis, the soil consists of approximately 33% silt, 60% sand and 7% gravel.

Table 15: Optimum Moisture Content and Maximum Dry Density Values for PCB-Contaminated Soil

Material (1)	Optimum moisture content (%) (2)	Maximum dry density (g/cm^3) (3)
20% Cement-Soil	21	1.38
50% Cement-Soil	21	1.42

B. PCB Analyses

Because the contaminated soil initially did not contain significant PCB concentration, transformer oil was added to the soil at the ratio of 5 ml of oil to 100 grams of soil to increase initial PCB concentration in the soil. The density of transformer oil was approximately 0.86 g/cm^3. Therefore, the concentration of oil in the soil was around 43,000 mg/kg. Oil concentration was high in the soil, so it was expected that PCB concentration of the soil would also be high. However, the analyses of the transformer oil yielded 39.6 mg/kg PCB as arochlor 1254. Some records of PCB analyses for a number of transformer oil showed that PCB concentration differs considerably.

Initial PCB concentrations in the soil were measured by gas chromatograph following microwave assisted solvent extraction based on U. S. EPA method 3546. In order to determine which arochlors exist in the soil as PCB, the standard solutions of arochlor 1016, 1221, 1232, 1242, 1248, 1254 and 1260 were injected. Results showed that the soil has arochlor 1254 as PCB and initial PCB concentration (Arochlor 1254) in the soil is 1.74 mg/kg.

The results of PCB analyses in TCLP and DWLP leachates are given in Table 16. As expected, arochlor 1254 was seen in the leachates as PCB. Higher cement addition resulted in less PCB concentrations in the leachates implying that application of S/S process to PCB-contaminated soil will be more effective with higher cement addition. Moreover, the effect of aggregate size on leachate quality was observed. Samples with finer aggregate sizes yielded higher concentrations in the leachates due to the increased surface area exposed to the leachant in the crushed samples. Thus, it was seen that the only effective mechanism for S/S of PCB was physical entrapment rather than chemical reactions. The U. S. EPA regulations allow wastes containing 50 to 500 ppm PCB to be disposed of in landfills. Such landfill sites must have hydraulic conductivity of liner or underlying soil less than 10^{-7} cm/s, attenuation layer at the bottom of the landfill and above the historical high groundwater table at least 15 m thick, and monitoring wells and leachate collection system. Landfilling of wastes with PCB levels of less than 50 ppm is not currently regulated. That is, these wastes can be disposed of in landfills permitted under Resource Conservation and Recovery Act (RCRA) or even solid waste landfills (Freeman, 1988).

Table 16: PCB concentrations in TCLP and DWL leachate of PCB-contaminated soil solidified at different cement ratios

Cement Ratio	PCB Concentration (μg/L)			
	1-2 mm		> 2mm	
	TCLP	Water	TCLP	Water
20%	30	14	18	6
35%	22	11	11	5

In order to assess leachate quality, the Drinking Water Standard of PCB, being 0.5 μg/L (Watts, 1998), was used. Following the U. S. EPA guidelines, i.e., using the magnifying factor of 100 to drinking water standard, gives maximum allowable concentration of PCB in the TCLP leachate as 50 μg/L. PCB concentrations measured in TCLP leachate (Table 14) are lower than this value, but 20 to 60 times higher than the drinking water standard. Calculated percent retention efficiency of PCB in the solidified/stabilized soil after TCLP and DWLP extractions are given in Table 17. Higher retention efficiencies were obtained with higher cement addition and samples of larger aggregate size.

Table 17: Percent retention efficiency of PCB concentration in S/S soil samples after TCLP and DWLP

Cement Ratio	Retained (%)			
	1-2 mm		> 2mm	
	TCLP	Water	TCLP	Water
20%	66	84	79	93
35%	75	87	87	94

C. Unconfined Compressive Strength and Hydraulic Conductivity Tests

Both hydraulic conductivity and unconfined compressive strength tests were performed on duplicate solidified/stabilized samples of PCB-contaminated soil. The results of these tests are given in Table 18. Results showed that PCB affected the strength development of portland cement, because the values of unconfined compressive strength values were much lower than those for mining waste and AOX containing sludge. Especially, unconfined compressive strength of solidified soil with 20% cement was just above the U. S. EPA standard of 350 kPa. Therefore, 20% cement addition was not enough for effective applications of S/S for PCB-contaminated soil. It seems that PCB in the soil interferes with the strength development or hydration reaction of cement. However, the unconfined compressive strength value of solidified soil with 35% cement added satisfies the U.S. EPA standard of 350 kPa recommended for disposal in landfills.

Table 18: Unconfined compressive strength (q_u) and hydraulic conductivity (K) values for PCB-contaminated soil samples solidified at different cement ratios

Property (1)	20% Cement (2)	35% Cement (3)
q_u, kPa	373	1340
K, m/s	1.1×10^{-9}	4.4×10^{-10}

As in the case of other waste types, hydraulic conductivity values of solidified PCB-contaminated soil decreased with higher cement addition. These conductivity values were lower than the U. S. EPA standard of 10^{-7} m/s required for disposal in landfills.

6. HEALTH AND SAFETY

Not applicable.

7. ENVIRONMENTAL IMPACTS

Not applicable.

8. COSTS

Not available.

9. CONCLUSIONS

S/S of mining waste was investigated for four cases: combinations of two different portland cement ratios (10% and 20%) and two different particle size distribution of plane waste (fine and coarse). For all cases of metals it was shown that the application of S/S produced acceptable results from a regulatory perspective. Unconfined compressive strength values were in the range of 1019 to 3250 kPa and hydraulic conductivity in the range of 1.04×10^{-9} to 2.1×10^{-9} m/s, which were below the U. S. EPA regulated values for landfilling. The effect of aggregate size on TCLP leachate quality was also investigated using in TCLP tests solidified samples crashed into two different aggregate sizes. Test results showed that S/S produced metal retention efficiencies in the solidified mass greater than 94%. In terms of the effect of particle size distribution of the plane mining waste, as a general trend, at the same cement-waste ratio leachate concentrations of fine waste samples were lower than those of coarse waste samples.

Technical criteria for the performance assessment of S/S require low leachate concentrations, low permeability and high unconfined compressive strength. For metal containing mining waste, since all cases produced acceptable unconfined compressive strength and hydraulic conductivity values in terms of regulatory compliance, leachate concentrations seem to be the most critical factor in assessing the effectiveness of S/S technology. Therefore, overall results indicate that the most suitable conditions for S/S of metal containing hazardous wastes occur when 10% cement is mixed with the plane waste consisting of nearly 75 % fine (silt and clay size) particles. However, the application of S/S for cadmium was not successful because leachate concentrations of cadmium exceeded the regulatory limits of the U. S. EPA. Therefore, for effective applications of S/S to the mining wastes containing high cadmium concentration ($\approx$1000 mg/kg), cement addition should be greater than 10%.

For the S/S of AOX containing pulp and paper sludge, it was observed that portland cement was highly effective in retaining AOX within solid matrix. Percent retention efficiency of solidified/stabilized AOX was 85%. However, AOX concentrations in the leachate were slightly above the regulated levels. Cement-mixing ratio and crashing the solidified samples into different aggregate sizes did not affect AOX concentration in leachate. There was only a slight decrease in leachate AOX concentrations with increasing cement addition. When the other technical criteria (unconfined compressive strength and hydraulic conductivity) were taken into consideration, they were consistent with the U.S. EPA standards. For successful application of S/S to pulp and paper sludge containing AOX concentration greater than 400 mg/kg, the cement ratio can be increased beyond 50% or other additives as adsorbent must be used besides portland cement.

S/S of PCB-contaminated soil gave questionable results. Despite low initial PCB concentration in soil (1.74 mg/kg), PCB concentrations in TCLP leachate from solidified/stabilized soil samples were relatively high (in the range of 11-30 μg/L). Percent retention efficiency of PCB in S/S samples ranged between 66% and 87% for different treatments. Higher PCB concentrations in the TCLP leachates of solidified samples with finer aggregate sizes indicated that the physical entrapment in the pores is the major retention mechanism for solid matrix and therefore chemical fixation of PCB is not taking place. At low cement additions, unconfined compressive strength of PCB-contaminated soil was much lower than those of mining waste and AOX containing sludge. So, it can be concluded that PCB oil had an inhibitory effect on the strength development of portland cement when cement ratio is low. Overall result indicate that the effective applications of cement-based S/S to PCB contaminated coarse textured soils are highly unlikely especially at PCB concentration levels as high as 50 to 500 ppm range and at cement ratios less than 35%. In this regard, higher cement ratio or other additives, such as industrial adsorbents, together with portland cement can be applied in order to obtain better leachate quality and thus more effective S/S of PCB in soils.

10. REFERENCES

1. AWWA-APHA. (1989). Standard Methods for the Examination of Water and Wastewater, 17th edition, USA.

2. Conner J. R. and Hoeffner S. L. (1998). “The History Of Stabilization/Solidification Technology”, *Critical Reviews in Environmental Science and Technology*, 28(4), 325-396.

3. Freeman, H. M. (1988). *Standard Handbook of Hazardous Waste Treatment and Disposal*. McGraw-Hill, New York.

4. Glasser, F. P. (1997). “Fundamental aspects of cement solidification and stabilization”, *Journal of Hazardous Materials*, 52, 151-170.

5. Infante, R. N., and Acosta, I. L. (1988). “Comparison of extraction procedures for the determination of heavy metals in airborne particulate matter by inductively coupled plasma-atomic emission spectroscopy”, *Atomic Spectroscopy*, 9(6), 191-194.

6. LaGrega, M. D., Buckingham, P. L., and Evans, J. C. (1994). *Hazardous Waste Management*, McGraw Hill, New York.

7. Porteus, A. (1985). *Hazardous Waste Management Handbook*. Butterworths & Co Publishers, London.

8. Smith M.A. (1998). Evaluation of Demonstrated and Emerging Technologies for the Treatment and Clean Up of Contaminated Land and Ground Water, NATO/CCMS Pilot Study, Phase II, Final Report.

9. U.S. EPA. (1982). “Guide To The Disposal Of Chemically Stabilized And Solidified Waste”, SW-872, Office of Water and Waste Management, Washington DC.

10. U. S. EPA. (1989). “International Waste Technologies/Geo-Con In-Situ Solidification/ Stabilization, Applications Analysis Report”.

11. U. S. EPA. (1992). "Silicate Technology Corporations Solidification/Stabilization Technology for Organic and Inorganic Contaminants in Soils, Applications Analysis Report".

12. Watts, R. J. (1998). *Hazardous Wastes, Sources, Pathways, Receptors*. John Wiley and Sons, New York.

13. Wiebusch, B., Ozaki, M., Watanabe, H., and Seyfried, C. F. (1998). "Assessment of leaching tests on construction material made of incinerator ash (sewage sludge): investigations in Japan and Germany", *Water Science and Technology*, 38(7), 195-205.

Project No. 10

Metal-Biofilm Interactions in Sulphate-Reducing Bacterial Systems

Location	**Project Status**	**Contaminants**	**Technology Type**
Under development in consortium's laboratories	Final Report	Metals	Biological treatment
Technical Contact	**Project Dates**	**Media**	
Prof. Harry Eccles BNFL, Research & Technology, Springfields, Preston, Lancashire PR4 0XJ, United Kingdom Tel: 44 1772 762566 Fax: 44 1772 762891 E-mail: he1@bnfl.com	Project accepted 1998 Final project report 1999	Effluents and ground water	
	Costs Documented?	**Project Size**	**Results Available?**
	No	Laboratory	Yes

Project 10 was completed in 1999.

1. INTRODUCTION

Sulphate-reducing bacteria (SRB) were developed to remove toxic heavy metals and radionuclides from liquid effluents and/or contaminated ground waters. The technology is currently at the laboratory scale to provide fundamental data to enable engineers to design better bioreactors. SRB technology for the removal of toxic heavy metals has been used on a limited number of occasions. In general, the bioreactors have been over-engineered thus increasing both the capital and operational costs and consequently the technology is not perceived as competitive. With intrinsic bioremediation, under anaerobic conditions, such as wetlands technology, SRB plays a key role in the sequestration of metals. It is not fully understood if this SRB role is complementary or pivotal. If the latter function predominates then understanding SRB-metal precipitation mechanisms could enable the wetlands to be better engineered/controlled leading to more effective in-situ treatment.

The aim of this project was to generate new fundamental data by:

1. Employing a purpose designed biocell
2. Generating fundamental metal precipitation data from this biocell
3. Investigating factors affecting growth of sulphate-reducing bacterial (SRB) biofilms
4. Quantification of important biofilm parameters on metal immobilization

2. SITE DESCRIPTION

The studies were carried out in the consortium's laboratories.

3. DESCRIPTION OF THE PROCESS

Biological processes for the removal of toxic heavy metals are presently less favored than their chemical/ physicochemical counterparts. Reasons for this are several; one of which is the inability to intensify the technology due to the lack of fundamental data. BNFL and its partners used a novel biofilm reactor to provide such information that can be used by the consortium's biochemical engineers and biofilm modelers to design better, smaller and more efficient bioreactors incorporating SRB technology.

These bacteria are capable of reducing sulphate ions in liquid waste streams to hydrogen sulphide, which with many toxic heavy metals will precipitate them from solution as their insoluble sulphides.

As the solubility products of these sulphides are very small the final treated effluent will meet the most stringent specification. Equally as the biological system is an active metabolic one the initial metal concentrations can be comparatively high i.e., a few hundred ppm.

The project commenced on the 1 April 1996 and was completed on the 31 March 1999.

4. RESULTS AND EVALUATION

At the outset of this project it was appreciated that consistent, reproducible transferable results were required from both of the laboratories (Westlakes Scientific Consulting [WSC] and the University of Dundee [UOD]) involved in the project. Equally biofilm characterization protocols needed to be developed/modified so that the SRB biofilms grown under a variety of conditions and challenged with several toxic heavy metals could be comprehensively examined.

A. Biocell Design and Operation

A key component of the project was the provision of sound laboratory data in reasonable time-frames. To satisfy these and other criteria a purpose designed biocell was constructed by a local specialist engineering company. Prior to manufacture the design of the biocell with respect to flow regimes for a variety of liquor flow-rates was simulated using CFD and subsequently verified by both WSC and UOD. Laminar flow was achieved throughout (>95%) of the biocell biofilm active region.

The biocell comprised of two chambers separated by a membrane. In some experiments a porous membrane was employed thus allowing a variety of experiments to be carried out which included for example:

1. The separation of carbon source, or sulphate or heavy metal from the SRB biofilm.
2. Transfer, by pressure manipulation, of carbon source, or sulphate through the membrane into the biofilm with the generated sulphide subsequently coming into contact with the metal solution.
3. The reverse of the above.

The biocell units were constructed in two sizes (lengths), a larger one (500 mm biofilm active length) and a smaller unit (100 mm biofilm active length). The longer biocell was largely used for growing the initial SRB biofilm on an appropriate membrane and dissected into lengths that could be accommodated by the smaller unit. Most of the metal precipitation studies were undertaken in these units.

The philosophy for this arrangement was the period for biofilm growth was not less than 14 days whereas metal precipitation studies took no more than 2 days to complete.

Factors Affecting Biofilm Growth

A major variable was the identity of the carbon/energy source used for culture. In general sulphate reduced per mol of carbon source consumed was in the order: lactate > ethanol > acetate. Organic nitrogen (e.g., a defined vitamin solution) also stimulated yield. However, a complex organic nitrogen source e.g., yeast extract did not further stimulate yield. The structure of the support material also affected biomass yield. Pore size stimulated yield between pore sizes of 20-100 μm. This appeared to primarily affect the area available for attachment.

Temperature (maximum growth at 30°C), and the substrate concentration also affected growth and sulphate reduction significantly and K_m values were determined. No effect was observed due to phosphate concentration, inorganic N concentration or support material or hydrophobicity. Prolonged culture led to deeper biofilms but the maximum active depth (shown by fluorescein diacetate-staining) remained at approximately 500 μm with deeper material appearing to be inactive.

B. Substrate Utilization

The biofilm flow cell (biocell) was a key element in this project. It allowed a defined area of biofilm to be incubated under defined conditions of rheology and nutrient supply by recirculating medium from a reservoir and samples of the recirculating medium can be removed for assay. Substrate-utilization was studied in the biocell as a closed system where a fixed quantity of medium was circulated and the substrate was depleted over time by the metabolic activities of the biofilm.

This system permitted measurement of the concentration and rate of use of substrates. Sodium lactate was rapidly utilized, producing acetate. Varying the concentrations over a 10- to 20-fold range and allowed determination of lactate utilization kinetics, this was carried out by personnel engaged on process modeling (K m @ 1,4 mM). Acetate was utilized very slowly by the biofilm culture and accumulated during experiments on lactate utilization as it was produced by SRB metabolizing lactate.

When acetate was supplied as the sole carbon/energy source, its rate of utilization and the accompanying sulphate reduction were almost undetectable so that no kinetic parameters could be determined. The low acetate utilization appeared to result from absence of acetate-degrading organisms from the mixed culture, probably as a result of selection by maintaining the culture on lactate as sole carbon/energy source. An acetate-utilizing mixed SRB culture was obtained, combined with the lactate-utilizing culture and the combined culture was maintained on mixed lactate and acetate as carbon/energy source. This combined culture utilized acetate considerably faster than the lactate-grown culture alone. However, it was not possible to fit a single set of kinetic parameters to the data.

As the addition of an acetate-utilizing culture led to increased acetate utilization, it appears that the very low rate of acetate utilization in the original culture was due to the absence of acetate-degrading organisms.

Effects of Metal Uptake on Biofilm Growth

Biofilms exposed to Cd or Cu in the growth medium accumulated the metal sulphides. Metal sulphide uptake was accompanied by increased content of protein and polysaccharide content of the biofilm as well as its increased thickness. The increase in polysaccharide was considerably greater than of protein, so that it appeared that extracellular polysaccharide was secreted in response to the accumulation of metal sulphides in the biofilm. The accumulated metal sulphides were concentrated in the upper part of the biofilm and resulted in increased biofilm thickness, but the depth of active (fluorescein diacetate-staining) biofilm remained the same (approximately 500 µm) in metal-loaded biofilms**.** Metal sulphide deposits could, however, overlie the active cells in metal-loaded biofilms, which indicates that these deposits did not obstruct diffusion of nutrients to the biofilm.

5. METAL PRECIPITATION STUDIES

5.1 Metal (Cd and Cu) Bioprecipitation

The kinetics and metal mass-balances of Cd and Cu bioprecipitation were studied using the biocell system. After flushing sulphide from the system, the appearance of soluble sulphide in the medium was rapid in the absence of metals but was delayed, in the presence of Cd or Cu. The apparent "shortfall" of sulphide was stoichiometric with the metal added to the medium, which was consistent with metal sulphide formation. However, not all of the metal sulphide formed was immediately precipitated, as some remained dispersed as colloidal material. A method of fractionating the metal into soluble, colloidal and precipitated fractions was developed and the time-course of formation and transformation of these fractions was investigated, this indicated that colloid flocculation to form precipitated solids was relatively slow compared to sulphide formation and appeared to be rate-limiting for the overall bioprecipitation process**.** Data on sulphate reduction, sulphide formation and colloid flocculation was used to parameterize and test a mathematical model that confirmed the rate-limiting nature of the flocculation step. In continuous culture, with a hydraulic residence time of 5 h, both Cd and Cu were precipitated. At metal concentrations used in batch experiments (250 μM), almost all metal was precipitated with a small colloidal phase and almost no remaining dissolved metal At 500 and 1000 μM metal a similar result was observed but with more of the metal remaining in solution and a similar percentage (approximately 5-10%) in the colloidal phase. It therefore appeared that the processes occurring in a continuous culture system were similar to those occurring in batch culture and that the residence time allowed significant flocculation of the colloidal material to take place. Although it is clearly an important component, the occurrence of a significant colloidal phase in metal sulphide bioprecipitation is a novel observation that does not appear to have been previously reported.

5.2 Iron Precipitation

The degree of iron sulphide formation by the biofilm (not previously exposed to FeSO4) was found to depend upon the initial FeSO4 loading of the medium, with a saturating concentration 0.5mM FeSO4. Under these conditions 0.86mg/cm^2 of Fe was taken up by the biofilm, but this represented only 16% of that in the system the rest precipitated in the system tubing and reservoir because of the biogenic S^- in solution.

6. MEMBRANE STUDIES

6.1 Permeable Membrane

Investigations into the flow characterization of the 2.5mm sintered polyallomer PorvairTM permeable membrane showed that a 20-day-old (mature) biofilm made the membrane less permeable, but there was sufficient fluid flow to allow the biocell to be effective at metal removal. Copper sulphate was used as the test heavy metal, fed through the membrane along with the lactate for biofilm metabolism. At high flow rates through the permeable membrane (>0.05mil/min/cm2) copper sulphide formed a suspension and appeared in the waste stream, whereas at lower flow rates, where the contact time between the metal and biofilm was increased, the amount of copper sulphide in the waste stream was reduced to insignificant levels.

6.2 Cross Flow Operation Using a Permeable Membrane

The biocell was set up with two channels for recirculating liquor separated by a permeable membrane, which supported the growing biofilm. The two recirculating liquor streams were only connected via the permeable membrane. Two main processes were envisaged to transport material between these streams bulk- phase transvection due to a pressure difference between the sides of the biocell and diffusion. Experiments varying the pressure difference across the membrane showed that solutes supplied in the bulk-phase liquor were transported proportionally to the exchange of volume, implying that transvection was the main mechanism. However, sulphide produced by the biofilm was approximately equally distributed between both sides of the biocell even at low-pressure differentials, which produced no bulk-phase movement. This indicated that the sulphide was transported out of the biofilm in both directions by diffusion. When a metabolically-active biofilm was grown on one side of the biocell and metal (Cd) solution was supplied on the other (sterile) side of the biocell, bioprecipitation of the Cd occurred, removing it from solution. Cd was not detected on the biofilm side of the cell so this arrangement, with the biofilm separated from the metal-containing stream by a membrane, permits separation of the metal-containing and nutrient streams reducing any environmental risks from discharge of BOD in the form of nutrients or of toxicity to the biofilm from unprecipitated metals.

7. MODELING STUDIES

7.1 Biofilm

A model of the biological phenomena occurring within the sulphate reducing bacterial biofilms, has been developed. The model is based upon the Generalized Repository Model (GRM) developed by BNFL. The mechanistic model takes into account a complex microbiology based upon Monod type Kinetic, and incorporates chemical speciation based on the PHREEQE geochemical speciation package. The biofilm code allows the modeling of eight bacterial groups. All microbial groups in each biofilm layer are subject to growth and decay. Microbial growth is modeled via two groups of reactions, energy generating reactions and biomass generating reactions. Bacterial growth and substrate removal is modeled using Monod kinetics, in which substrate removal is related to biomass growth through the yield coefficient. Changes to the bulk chemistry due to microbial activity within the code are utilized as input data by the chemical speciation component of the code, PHREEQE.

The main roles of PHREEQE are the modeling of mineral precipitation and dissolution, speciation of dissolved species, and calculation of the ambient pH. The PHREEQE database has been modified to include lactate and acetate species, which are of specific interest to this project. Species diffuse into the biofilm and an equilibrium is reached between adjacent compartments, (i.e., another biofilm layer or, in the case of the upper biofilm layer, the bulk liquid phase). Microbial degradation changes the concentration of species in the biofilm layers, and compounds diffuse in and out of the layers tending towards equilibrium. Whilst this is occurring the speciation component of the code determines the reaction path of the released species.

Speciation is carried out in the bulk liquid phase, and each of the individual biofilm layers. The rate at which microbial degradation and speciation occur determines the compartment in which the minerals precipitate Species which become incorporated in a mineral phase, by precipitation, remain in that compartment and are not subject to diffusion. The inclusion of advection allows a series of model cells to be connected, allowing a range of experimental and environmental situations to be modeled. After each time step (time taken for speciation, diffusion, and microbiology), species are able to enter and leave the model cells, via adjacent model cells, or an external route.

Microbial growth within each layer is dependent on the diffusion of substrate. The model is based upon a single, or series of model cells, containing a gas phase, bulk liquid phase, biofilm and a substratum.

The model has been success fully applied to results produced by the University of Dundee. It was possible to model the utilization of lactate and sulphate within the biofilm, and the precipitation of cadmium sulphide with a high degree of success. At present the model has had a limited application, as modeling the BNFL biocell experiments has not utilized the bulk of the models capabilities.

A number of biofilm models are reported in current literature, however none include an extensive microbiology and such a comprehensive speciation component. The model may be applied to further modeling tasks in the future, taking advantage of the full extent of it capabilities.

7.2 Bioreactor Configuration

From the point of view of engineering design, the project has disclosed the following new information:

A. Kinetics

At the start of the project, only one paper was available on tentative reaction kinetics in SRB systems. This project has shown that:

1. Sulphide production is zero order in sulphate concentration and exhibits a Monod rate dependence on carbon substrate composition (ignoring complications from acetate utilization),

2. The biofilm kinetics do not alter substantially as the film grows, supporting modeling work presented in the literature on non-SRB systems that there is a constant, active biofilm thickness,
3. Sulphide production rate does not appear to be affected by the adsorption of insoluble sulphides, and kinetics are dependent on intrinsic kinetics with little effect of diffusional mass transfer in the film,
4. As a consequence of the above, a simple form for the local kinetics at a point in a reactor is possible, thereby reducing the computational complexity of previous literature models.

B. Metal Precipitation

The form of the precipitation of metal sulphide is very important as it exerts a profound effect on reactor performance and the design of ancillaries to remove insolubles from the reactor outlet stream. This was not realized at the outset of the project and has not, hitherto, been discussed or analyzed in the literature. Nonetheless, the experimental and theoretical work in the project has:

1. Allowed estimates of the rate of flocculation of colloidal material to be made (which do not appear to be substantially affected by the presence of the biofilm),
2. Allowed estimates of the rate of biofilm capture of colloidal material to be made, and
3. Has shown the conditions under which metal precipitation occurs predominantly either within the biofilm or in the free solution outside the film.

C. Reactor Modeling

The few reactor models for SRB systems in the literature have used very complex biofilm kinetics and have not considered practical issues such as flocculation and precipitation. A simple reactor model has been constructed which could be used immediately to interpret the results from a pilot-scale reactor. It demonstrates that very careful process control is important in order to achieve the stringent targets with regard to both soluble sulphide concentration and soluble metal concentration in the discharged stream. The model indicates the great sensitivity of the quality of the discharged stream to changes in key parameters.

Project No. 11

Predicting the Potential for Natural Attenuation of Organic Contaminants in Groundwater

Location Operational coal tar processing and organic chemicals manufacturing plant, West Midlands, U.K.	**Project Status** Final report	**Media** Groundwater	**Technology Type** Intrinsic bioremediation, natural attenuation
Technical Contact Dr. Steve Thornton, Groundwater Protection & Restoration Group Dept. of Civil & Structural Engineering University of Sheffield, Mappin St. SHEFFIELD S1 3JD United Kingdom Tel: 0114 222 5744 Fax: 0114 222 5700 E-mail: s.f.thornton@sheffield.ac.uk	**Project Dates** Accepted 1998 Final Report 1999	**Contaminants** Coal tars, phenol, cresols, xylenols, BTEX	
	Costs Documented? Not applicable	**Project Size** Not applicable	**Results Available?** Yes

Project 11 was completed in 1999.

1. INTRODUCTION

Natural attenuation is an emerging technology, which uses natural biological and chemical processes occurring in aquifers to reduce contaminants to acceptable levels. The technology has been used successfully in shallow North American aquifers but has not been developed for the deep, fractured, consolidated aquifer systems found in the U.K. 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 primarily evolved from studies of petroleum hydrocarbon and chlorinated solvent spills at sites in North America. However, 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 U.K. has a legacy of contaminated industrial sites located on deep, consolidated, dual-porosity aquifers and groundwater pollution from these sites often results in the development of complex plumes.

The application of natural attenuation 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.

Coal-gasification plants are an important source of soil and groundwater pollution in the U.K. 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 U.K. aquifers is poor.

2. BACKGROUND

The research site is an operational coal-tar processing and phenols manufacturing plant, constructed in 1950, and situated in the U.K. West Midlands. The plant is located on a deep, unconfined, fractured, Permo-Triassic sandstone aquifer and has contaminated the groundwater with a range of phenolic compounds, including phenol, cresols, xylenols and BTEX, some at concentrations up to 12,500 mg l^{-1}. The aquifer is naturally aerobic, calcareous at depth and contains abundant Fe and Mn oxides as grain coatings. Groundwater levels are shallow (typically <5 mbgl) and the aquifer is 250 m thick in the vicinity of the site. Groundwater flow is 4-11 m y^{-1}. The current volume of the plume is about 3 million m^3. The total concentration of organic compounds in the plume source area is presently 24,800 mg l^{-1}, including 12,500 mg 1^{-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 449 mg l^{-1}. There is no information to indicate when spillages stopped, although the plume remains anchored by a strong source. The only receptor at risk is a public supply borehole, located approximately 2 km west of the plant and >100 y travel time from the present plume.

The project objectives are (a), to understand processes controlling the natural attenuation of a complex mixture of organic pollutants in a U.K. sandstone aquifer, (b), to develop practical techniques to estimate the potential for natural attenuation and (c), to understand the value of intervening to increase attenuation. The key research issues are (a), estimating the timing and duration of degradation, (b), understanding the degradation processes and potential inhibitors, (c), quantifying the role of mineral oxidants in degradation, (d), assessing the supply of soluble electron acceptors from dispersion and diffusion at the plume fringe, and (e), assessing the contribution of fermentation to degradation.

The project is funded primarily by the UK Engineering and Physical Sciences Research Council and Environment Agency, with additional contributions from the UK Natural Environment Research Council through affiliated projects. The project began in September 1996, in collaboration with the British Geological Survey, Institute of Freshwater Ecology and University of Leeds, and is 3 years duration. Industrial collaborators include Laporte Inspec, BP, SAGTA and Aspinwall & Co.

3. TECHNICAL CONCEPT

Simultaneous field investigations, laboratory studies and reactive transport modeling have been initiated and are ongoing. The field studies have focused on characterization of the baseline groundwater hydrochemistry and microbiology in the plume. This was undertaken to identify spatial and temporal variations in the distribution of contaminants, redox processes, dissolved gases, microbial population activity and diversity. Two comprehensive groundwater quality surveys have been completed for the suite of 25 monitoring boreholes installed by consultants responsible for the site investigation (Aspinwall & Co., 1992). A basic conceptual process model of contaminant attenuation was developed with this data. High-resolution multilevel groundwater samplers (MLS) have been developed and installed in the plume at 130 m and 350 m from the site, to depths of 30 m and 45 m below ground level, respectively. These devices provide a vertical profile through contaminated and uncontaminated sections of the aquifer at a level of detail unobtainable with the existing borehole network. The MLS boreholes have been used to quantify solute fluxes, degradation rates, redox processes, and identify environmental controls on degradation in the plume. The MLS have been sampled at quarterly intervals over a year to monitor changes in plume redox conditions and microbial population dynamics in response to water table fluctuations in the aquifer. A rock core was recovered anaerobically from the aquifer, adjacent to one of the MLS boreholes, to provide material as inoculum for laboratory process studies, for examination of microbial ecology, for analysis of metal oxide and silicate mineralogy, and for stable isotope characterization of reduced sulphide and carbonate minerals.

Laboratory microcosm studies using acclimated groundwater and aquifer sediment are in progress to examine the degradation rates of phenolic mixtures under the range of redox and environmental conditions found in the plume. The scope of these process studies is wide and includes an assessment of degradation coupled to different aqueous and solid phase oxidants, identifying the contribution of fermentation to degradation and understanding the broad controls on degradation (e.g., oxidant bioavailability and contaminant toxicity). Different redox systems were established in the microcosms under different contaminant concentrations in order to understand the timing and extent of degradation. Initially, aquifer sediment incubated under different redox conditions in boreholes at the site was used as inocula in the microcosms. Additional process studies are now in progress using rock core material recovered from the aquifer. These will examine the spatial variability in aquifer degradation potential, and quantify the bioavailability of mineral oxidants in degradation along a vertical profile through the plume. Microbiological analysis of groundwater and aquifer sediment samples has focused on understanding the spatial and temporal variability in the diversity and activity of indigenous microbial populations. These variations have been compared for the range of redox conditions and contaminant concentrations found in the plume, to refine the process model developed from the hydrochemical data and to understand the broad environmental controls on microbial ecology and aquifer potential for contaminant degradation.

Reactive transport modeling of biodegradation processes in the plume is ongoing. An initial modeling study was undertaken with the biodegradation code, BIOREDOX, to test the conceptual process model of the plume and to identify additional modeling objectives. Further transport modeling is now underway in collaboration with the University of Waterloo in Canada, using a more advanced code. The necessary parameter values, rate data and processes required for modeling are obtained from the laboratory and field studies. This will provide an independent assessment of the utility of the approach in predicting contaminant fate at field scale.

4. ANALYTICAL APPROACH

Groundwater samples have been collected, anaerobically, for analysis of organic contaminants, dissolved gases (e.g., N_2, CO_2, CH_4), major cations, major anions, organic and inorganic (e.g., total inorganic carbon, Fe^{2+}, Mn^{2+}, S^{2-}) metabolites of phenolic compound degradation, nutrients, $^{34}S/^{32}S\text{-}SO_4$, $^{34}S/^{32}S\text{-}S^{2-}$, $^{13}C/^{12}C\text{-}CO_3^{2-}$, $^{18}O/^{16}O\text{-}SO_4$, organically-complexed and organically-uncomplexed Fe, and microbiological parameters. Samples have been collected concurrently for analysis of these determinands on each groundwater survey, to provide time-series data for comparison. Geochemical modeling of the groundwater quality data has been completed to identify potential sinks for inorganic products of biodegradation and to refine a carbon mass balance for the plume.

Microbiological analysis has included enumeration of total and culturable bacteria. Direct measures of *in situ* degradation potential have been made on groundwater and aquifer sediment samples by stimulation with NO_3 and addition of radiolabeled phenol compounds and other aromatic hydrocarbons. Microbial diversity has been assessed after inoculation of samples with different nutritional tests.

Rock core samples have been analyzed for oxidation capacity (OXC) and mineral phases (e.g., iron sulphides, metal oxides, carbonates and aluminosilicates). Permeameter tests and analyses of mineral phase $^{34}S/^{32}S\text{-}S^{2-}$ and $^{13}C/^{12}C\text{-}CO_3^{2}$- stable isotopes have also been performed on core samples.

5. RESULTS

The range of redox and microbial processes identified in the plume has demonstrated the aquifer potential for aerobic and anaerobic degradation of the organic contaminants. Contaminant degradation is occurring under aerobic, nitrate-reducing, iron/manganese-reducing, sulphate-reducing, and methanogenic conditions, at contaminant concentrations up to 24,000 mg L^{-1}. Degradation rates and microbial activity are highly variable and are correlated with contaminant concentrations and electron acceptor availability in the plume. There is increased microbial activity, diversity and degradation at the plume fringe, in response to the increased flux of dissolved oxygen and nitrate from the background groundwater and dilution of contaminant concentrations. The supply of aqueous oxidants and dilution of contaminants are controlled by mechanical dispersion at the plume fringe. The mixing zone over which this dispersion occurs is relatively small (2 m) for the plume under study. A carbon and electron acceptor mass balance for the plume has constrained the plume source term and suggests that degradation has not been significant within much of the plume (Thornton *et al.*, 1998). The mass balance suggests that dissolved oxygen and nitrate, supplied by dispersion, are more important for contaminant mass turnover in the plume than other degradation processes. The stable isotope studies show that a contaminant threshold concentration exists for the initiation of sulphate reduction in the plume, although other degradation processes appear relatively insensitive to the organic pollutant load.

6. HEALTH AND SAFETY

Not available.

7. ENVIRONMENTAL IMPACTS

Not available.

8. COSTS

Not available.

9. CONCLUSIONS

A combination of methodologies has been developed to assess the potential for natural attenuation of organic contaminants at this site. These methodologies include theoretical approaches and practical, field-based, technology which provides an improved framework for understanding the behaviour of complex plumes in aquifers. Contaminant fate in this aquifer system is controlled by a complex plume source history and spatial variations in the aquifer degradation potential, as influenced by contaminant concentration and the bioavailability of oxidants. Source history has a greater impact on contaminant concentrations in this aquifer than degradation processes. The field and laboratory studies show that contaminant mass loss can be demonstrated for the range of environmental conditions found in the plume. However, although the phenolic compounds are biodegradable and the aquifer is not oxidant limited, the plume is likely to grow under the present conditions. 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 increase only after increased dilution of the plume.

10. REFERENCES

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

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

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

4. 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.

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

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

7. 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.

Project No. 12

Treatability Test for Enhanced In Situ Anaerobic Dechlorination

Location	**Project Status**	**Media**	**Technology Type**
Cape Canaveral Air Station, FL Naval Air Station Alameda, CA Fort Lewis, WA Camp Lejeune, SC	Demonstration complete Demonstration complete Demonstration complete Demonstration in progress	Groundwater	In situ bioremediation

Technical Contact	**Project Dates**	**Contaminants**	
Capt. Dave Kempisty AFRL/MLQ 139 Barnes Drive, Suite 2 Tyndall AFB, FL 32403 Tel: 850-283-6126 Fax: 850-283-6064 E-mail: david.kempisty@tyndall.af.mil Andrea Leeson DoD SERDP/ESTCP Cleanup Program Manager 901 N. Stuart Street, Suite 303 Arlington, VA 22203 Tel: (703) 696-2118 Fax: (703) 696-2114 E-mail: andrea.leeson@osd.mil	Accepted 1999 Final Report 2002	Tetrachloroethylene (PCE), trichloroethylene (TCE), dichloroethene (DCE), vinyl chloride	
	Costs Documented?	**Project Size**	**Results Available?**
	Spring 2002	Field Treatability Testing	Spring 2002

The information in this project summary is current as of January 2002.

1. INTRODUCTION

Chloroethene compounds, such as tetrachloroethene (PCE) and trichloroethene (TCE), have been widely used for a variety of industrial purposes. Past disposal practices, accidental spills, and a lack of understanding of the fate of these chemicals in the environment have led to widespread contamination at U.S. Department of Defense (DoD) and industrial facilities. Enhanced anaerobic dechlorination is a very promising bioremediation treatment approach for remediating chlorinated ethene-contaminated groundwater. The goal of this effort is to develop and validate a comprehensive approach for conducting a treatability test to determine the potential for applying reductive anaerobic biological in situ treatment technology (RABITT) at any specific site. A treatability protocol has been written (Morse, 1998) and will be applied to five DoD chlorinated solvent contamination sites in the United States. Based on the field test results, the protocol will be revised as needed upon completion of the effort.

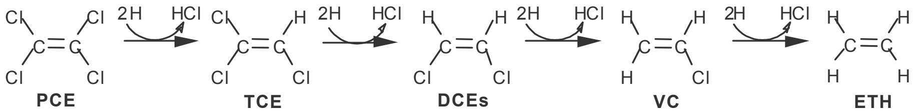
2. BACKGROUND

Because both PCE and TCE are stable compounds that resist aerobic degradation or require the presence of an electron-donating co-contaminant for anaerobic transformation, these compounds tend to persist in the environment. However, in reductive systems, highly oxidized contaminants (e.g., PCE) can be utilized as electron acceptors. RABITT attempts to stimulate this reductive pathway by supplying excess reduced substrate (electron donor) to the native microbial consortium. The presence of the substrate expedites the exhaustion of any naturally occurring electron acceptors. As the natural electron acceptors are depleted, microorganisms capable of discharging electrons to other available electron acceptors, such as oxidized contaminants, gain a selective advantage.

The reductive dechlorination of PCE to ethene proceeds through a series of hydrogenolysis reactions shown in Figure 1. Each reaction becomes progressively more difficult to carry out.

Figure 1: Reductive Dechlorination of PCE

The selection of an appropriate electron donor may be the most important design parameter for developing a healthy population of microorganisms capable of dechlorinating PCE and TCE. Recent studies have indicated a prominent role for molecular hydrogen (H_2) in the reductive dechlorination process (Holliger et al., 1993; DiStefano et al., 1992; Maymo-Gatell et al., 1995; Gossett et al., 1994; Zinder and Gossett, 1995). Most known dechlorinators can use H_2 as an electron donor, and some can only use H_2. Because more complex electron donors are broken down into metabolites and residual pools of H_2 by other members of the microbial community, they may also be used to support dechlorination (Fennell et al., 1997; Smatlak et al., 1996; DiStefano et al., 1992).



The rate and quantity of H_2 made available to a degrading consortium must be carefully engineered to limit competition for hydrogen from other microbial groups, such as methanogens and sulfate-reducers. Competition for H_2 by methanogens is a common cause of dechlorination failure in laboratory studies. As the methanogen population increases, the portion of reducing equivalents used for dechlorination quickly drops and methane production increases (Gossett et al., 1994; Fennel et al., 1997). The use of slowly degrading nonmethanogenic substrates will help prevent this type of system shutdown.

Because of the complex microbial processes involved in anaerobic dechlorination, thorough site characterization and laboratory microcosm testing are an important part of the RABITT protocol. The protocol presents a phased or tiered approach to the treatability test, allowing the user to screen out RABITT in the early stages of the process to save time and cost. The protocol guides the user through a decision process in which information is collected and evaluated to determine if the technology should be given further consideration. RABITT would be screened out if it is determined that site-specific characteristics, regulatory constraints, or other logistic problems suggest that the technology will be difficult or impossible to employ, or if competing technology clearly is superior.

The first phase of the treatability test includes a thorough review of existing site data to develop a conceptual model of the site. The protocol contains a rating system that can be used to assess the suitability of a site for RABITT testing. The rating system is based on an analysis of the contaminant, hydrogeologic, and geochemical profiles of the site. The decision to proceed with the RABITT screening process should be supported by data indicating that the site meets the requirements for successful technology application. The second phase of the approach involves selecting a candidate test plot location within the plume for more detailed site characterization. Characterization activities will examine contaminant, geochemical, and hydrogeologic parameters on a relatively small scale to determine the selected location's suitability as a RABITT test plot. Based on the information generated during the characterization of the test plot, a decision is made to proceed to phase three of the treatability study, which consists of conducting laboratory microcosm studies. The microcosm studies are conducted to determine what electron donor/nutrient formulation should be field-tested to provide optimum biological degradation performance. If the results from the microcosm testing indicate that reductive dechlorination does not occur in response to the addition of electron donors and/or nutrients, the technology is eliminated from further consideration. The fourth and final phase of the treatability test entails field testing the electron donor/nutrient formulation determined in the laboratory microcosm tests to be most effective for supporting biologically mediated reductive dechlorination. The data from this phased treatability test indicate the potential for the microbiological component of RABITT and are used to make the decision to proceed to pilot-scale or full-scale implementation of RABITT.

This effort consists of applying the protocol to five chlorinated solvent contamination sites. Currently the field treatability test systems are operating at two locations, Cape Canaveral Air Station, FL, and Naval Air Station Alameda, CA. Microcosm studies will begin in August 1999, using contaminated aquifer material from a site at Ft Lewis, WA which is the proposed location for site number three. The fourth and fifth field locations are yet to be determined.

3. ANALYTICAL APPROACH

A summary of soil and groundwater analytes is presented here. For detailed information on sample collection techniques or analytical methods, please refer to Morse, et al. 1998.

A. Site Characterization Activities

Soil cores are visually examined for soil type and stratigraphy. In addition, soil core subsamples are sent to an off-site laboratory and analyzed for VOCs, TOC, and Total Iron. Groundwater samples are analyzed for the following parameters: dissolved oxygen, temperature, pH, Fe^{+2}, conductivity, chloroethenes, dissolved organic carbon, ammonia, CH_4, C_2H_4, C_2H_6, NO_3, NO_2, SO_4, Cl, Br, alkalinity, and total iron.

B. Performance Monitoring of the Field Test Cell

Table 1 presents the performance monitoring parameters and their measurement frequency during field-testing.

Table 1: Performance Monitoring Parameters

Parameter	Measurement Site	Measurement Frequency
TCE, *cis*-DCE, VC, ethene	Lab	Initial, baseline, and biweekly
Volatile Fatty Acids (electron donor)	Lab	Initial, baseline, and biweekly
Bromide	Field and Lab	Initial, baseline, and biweekly
Dissolved Oxygen	Field	Initial, baseline, and biweekly
pH	Field	Initial, baseline, and biweekly
Conductivity	Field	Initial, baseline, and biweekly
Fe^{+2}	Field	Initial, baseline, and biweekly
CH_4, C_2H_4, C_2H_6	Lab	Baseline and monthly
NO_3, NO_2, SO_4, Cl	Lab	Baseline and monthly
Alkalinity	Lab	Baseline and monthly

4. RESULTS

4.1 Site 1: Cape Canaveral Air Station, FL

Description: Facility 1381, the Ordnance Support Facility at Cape Canaveral Air Station, contains a shallow, 110-acre volatile organic compound (VOC) plume consisting primarily of TCE, DCE, and VC. Improper disposal of solvents used for cleaning and degreasing operations contributed to this groundwater contamination plume. Field data suggest that TCE is naturally being dechlorinated to DCE and subsequently to VC. Each of these contaminants has been detected in a surface water body adjacent to the site.

The geology at the site is characterized by poorly sorted coarse to fine sands and shell material from ground surface to approximately 35 ft below ground surface (bgs). From approximately 35 to 50 ft bgs, sands show a decrease in grain size and the silt and clay content increases. From 48.5 to 51 ft bgs, a continuous clay unit appears to underlie the entire area at Facility 1381. Groundwater at the site is very shallow, generally ranging between 4 and 7 ft bgs. The hydraulic conductivity for the shallow groundwater has been determined to be approximately 88.7 ft/day. The pH of the groundwater ranged from 6.87 to 8.14 and conductivity readings ranged from 464 to 5,550 µmhos/cm. The groundwater flow velocity has been calculated to be 0.21 ft/day. The suspected source area contains high levels of TCE (up to 342 mg/L), but TCE concentrations drop off quickly and only DCE and VC are detected towards the edges of the plume.

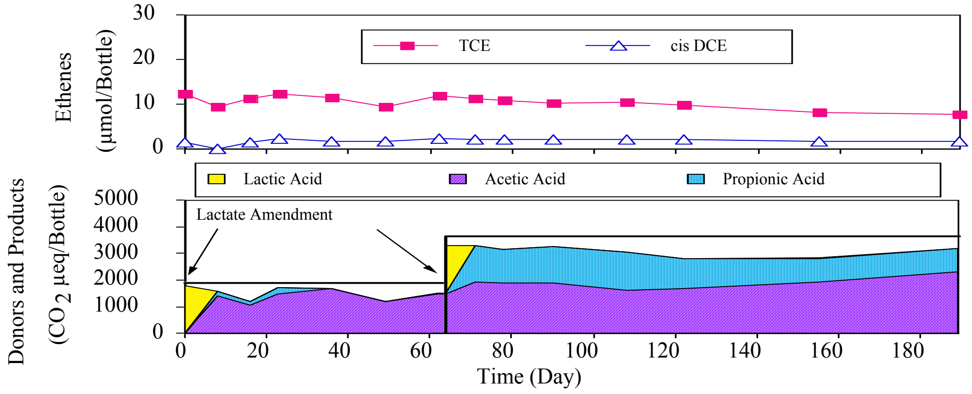
A. Microcosms

Microcosm studies at Cape Canaveral showed that all organic electron donors evaluated (lactate, butyrate, propionate, benzoate, and yeast extract amendment) promoted enhanced dechlorination of the 2 mg/L TCE, 10 mg/L cDCE and 1.5 mg/L VC present in the site groundwater. Lactate was selected for the electron donor to be used in the field-testing.

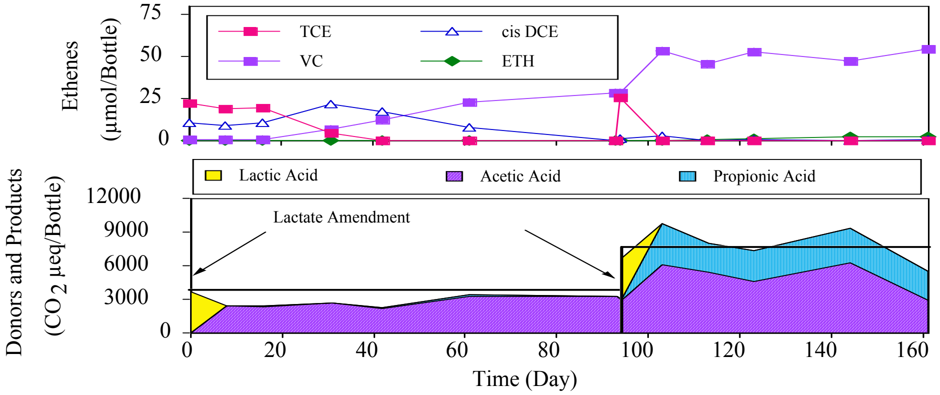
Figure 2 illustrates lessons learned from conducting microcosm studies. Upon the addition of lactate and vitamin B_{12} with no yeast extract, levels of TCE and cDCE show no significant signs of reduction. Alternatively, the addition of yeast extract along with lactate and vitamin B_{12} facilitated the onset of and completion of the dechlorination process.

Figure 2: Degradation of Chlorinated Compounds under Various Conditions: Cape Canaveral Air Station Aquifer Material

CCAS Microcosm 5C-II (GPW09/10) Lactate + B_{12}



CCAS Microcosm 5D-I (GPW06) Lactate +YE + B_{12}(Triplicates Similar)



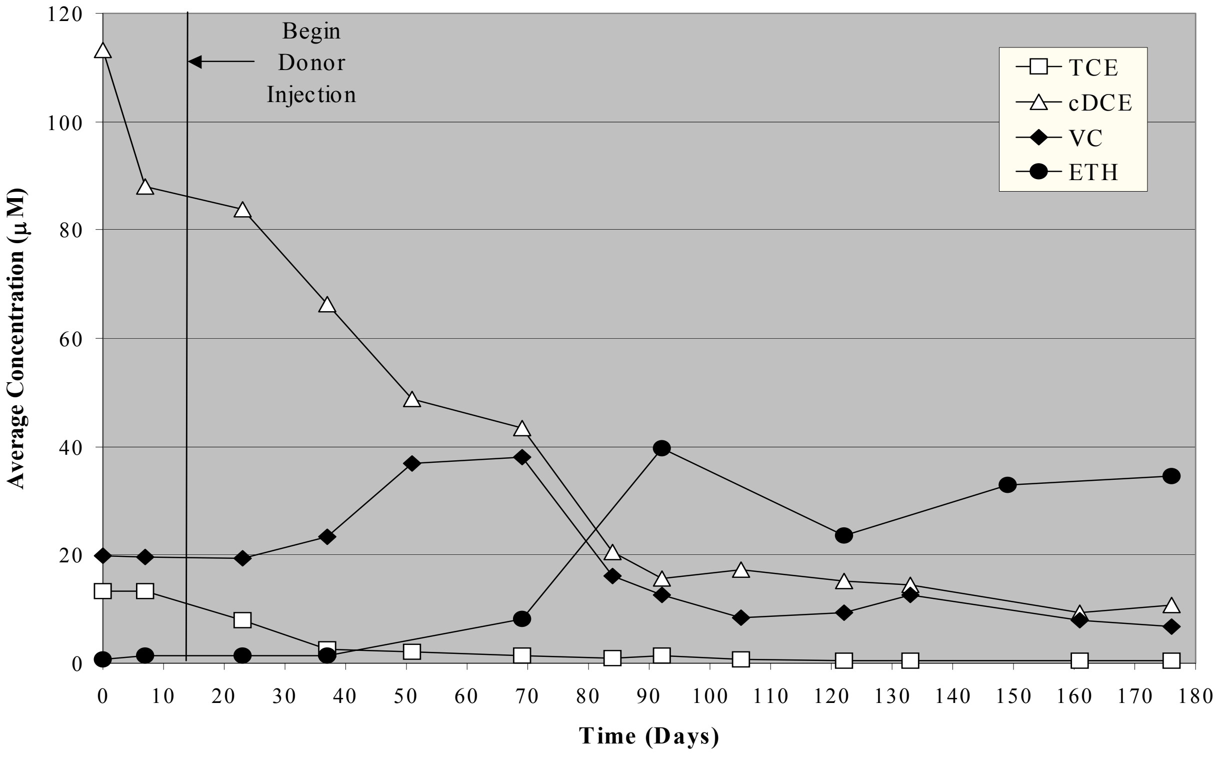
B. Field Study

The standard RABITT design was modified for the site at Cape Canaveral Air Station in order to meet the State of Florida Underground Injection Control regulatory requirements. This regulation does not allow for reinjection of contaminated groundwater. The objective of the modified system was to allow for effective delivery and distribution of nutrients and electron donors and to provide for extensive monitoring and hydraulic control, without pumping groundwater aboveground. The modified system was installed at Facility 1381 in March 1999 and operated for six months.

The modified design consisted of two communicating wells, a series of 13 tri-level groundwater monitoring probes, and upgradient and downgradient monitoring wells. The system wells are a dual screen design, with one operating in an upflow mode and the other in a downflow mode. Each well was screened within two distinct zones (10-12.5 and 17.5-20 ft bgs). The wells are placed close enough to affect each other with the effluent from one well feeding the other. This results in groundwater circulation that can be used to mix and distribute the electron donor/nutrient formulation. Tri-level monitoring points were screened in three zones that covered similar depths and an intermediate zone. The monitoring probes were positioned around the treatment cell to provide three-dimensional data that was required to track the tracer and added electron donor/nutrients, calculate mass reductions during treatment, and evaluate gains and losses from the treatment cell through background groundwater migration. The monitored plot dimensions were 39 ft by 10 ft.

After initial tracer testing established the site hydrological conditions, lactic acid was injected into the communicating well system to maintain an initial groundwater concentration of 3 mM lactate. The total system pumping rate was approximately 2,880 gal/day (7.6 L min).

Figure 3: Degradation of Chlorinated Compounds during Field Testing at Cape Canaveral



Cape Canaveral field-testing showed rapid dechlorination of TCE and cDCE to VC, followed by slower subsequent dechlorination to ethene under the established sulfate reducing to methanogenic conditions (Figure 3). Molecular probing indicated the presence of a dechlorinating organism similar to *Dehalococcoides ethenogenes*, an organism that has been shown to promote complete dechlorination with slow removal of VC. The treatment demonstrated reduction of TCE, cDCE, and VC by 88.7%, 90.6%, and 66.3%, respectively. The ethene concentration increased significantly to approximately 0.04 mM, but good molar balances were not possible due to diffusion. Overall, there was reasonable agreement between laboratory microcosm and field results.

4.2 Site 2: Naval Air Station Alameda, CA

A. Site Description

Building 360 (Site 4) at Naval Air Station Alameda was selected for the second demonstration. This building has been used as an aircraft engine repair and testing facility, and consisted of former machine shops, cleaning areas, as well as plating and welding shops and parts assembly areas. Solvents used in the cleaning shop of Building 360 have included a mixture of 55% PCE and other chemicals such as dichlorobenzene, methylene chloride, toluene and 30 to 70% solutions of sodium hydroxide. Site characterization activities performed by the facility revealed elevated levels of chlorinated solvents, primarily TCE (24 mg/L), DCE (8.6 mg/L), and VC (2.2 mg/L), between 5.5 and 15.5 feet bgs.

Depth to groundwater in the Building 360 area ranges between 4.4 feet and 6.5 feet bgs. Aquifer testing yielded hydraulic conductivity values from 1.22×10^{-3} to 3.86×10^{-3} cm/sec. The estimated groundwater flow is very low at only 1.1×10^{-5} cm/sec or 11.4 ft/year. It appears that groundwater in this area is very nearly stagnant.

B. Microcosms

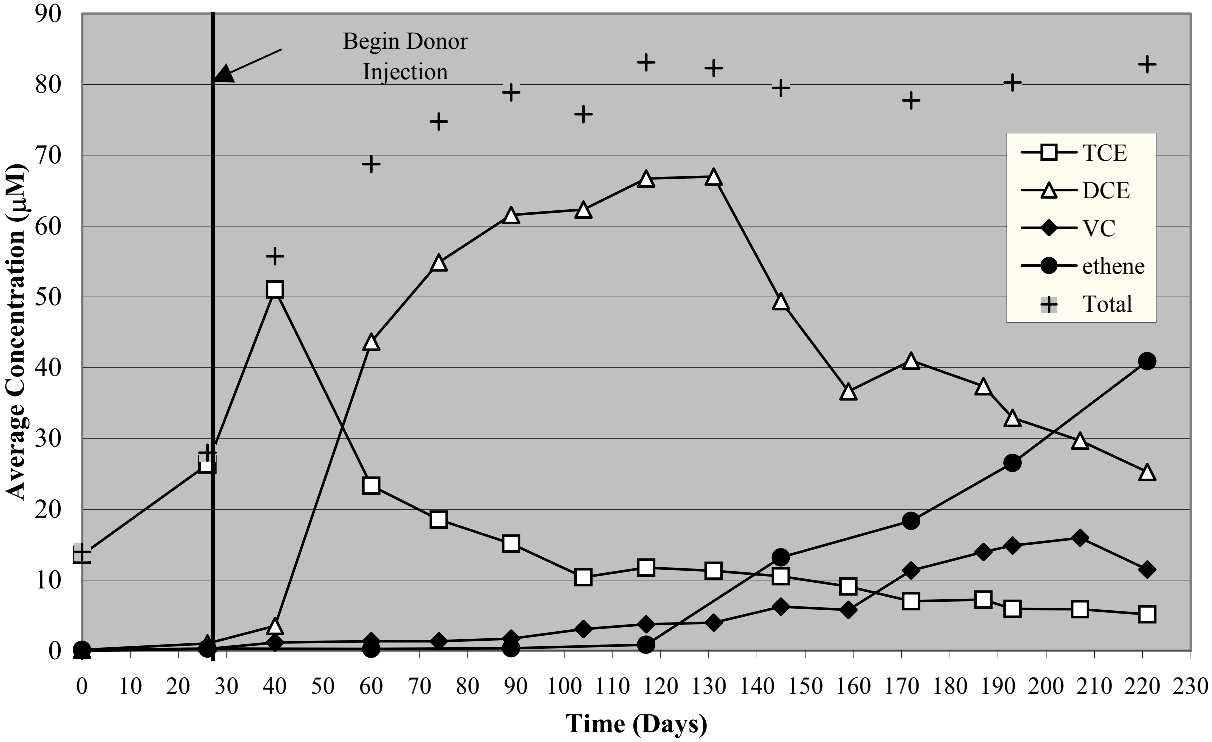
Microcosms showed that all electron donors tested except benzoate promoted enhanced dechlorination of TCE. Butyrate was chosen for field injection because of a shorter lag time associated with stimulating dechlorinating activity. TCE was rapidly dechlorinated to ethene under the established sulfate reducing to methanogenic conditions when supplied with a constant 3 mM supply of butyrate in the injected groundwater obtained from the supply well. Molecular probing to date has been negative for *D. ethenogenes*; however, recent data indicates that a closely related species may be present at the site.

C. Field Study

After baseline sampling and tracer testing, injection of butyric acid began in June 1999 using a flow through system. The field test involved an upgradient injection well and downgradient extraction well with aboveground recirculation. The injection well was supplemented with TCE-contaminated groundwater from a separate supply well outside the influence of the 3-ft by 15-ft monitored plot. The injection, extraction, and nine monitoring wells were all screened between 24 and 27 ft bgs. The total pumping rate for the system was 236 gal/day (0.62 L/min). Butyric acid and yeast extract were added to maintain initial in situ concentrations of 3mM and 20 mg/L respectively.

Injected groundwater contained average TCE, cDCE, and VC concentrations of 81.7 μM, 7.0 μM, and 3.4 μM respectively. By the end of the demonstration, the average TCE concentration observed in the treatment zone had been reduced by 94% despite the continuing input of TCE (Figure 4). In addition, both cDCE and VC were on the decline; ethene levels were steadily increasing and accounted for approximately half of the total chloroethene concentration. On average, 87% of injected chloroethenes could be accounted for during sampling events. Good agreement between microcosm and field results was also observed for the Alameda site.

Figure 4: Degradation of Chlorinated Compounds during Field Testing at NAS Alameda



4.3 Site 3: Fort Lewis, WA

A. Site Description

The East Gate Disposal Yard (EGDY) covers approximately 29 acres at Ft Lewis, WA. Aerial photographs indicate that between 1940 and 1971 the EGDY was used as a storage and disposal site for various solid and liquid wastes. The photographic evidence shows that the wastes were disposed of in large trenches and pits and that, on occasion, the waste materials were burned. Waste materials disposed of at the EGDY include TCE and petroleum, oil, and lubricant wastes from equipment cleaning and degreasing activities conducted at the Fort Lewis Logistics Center.

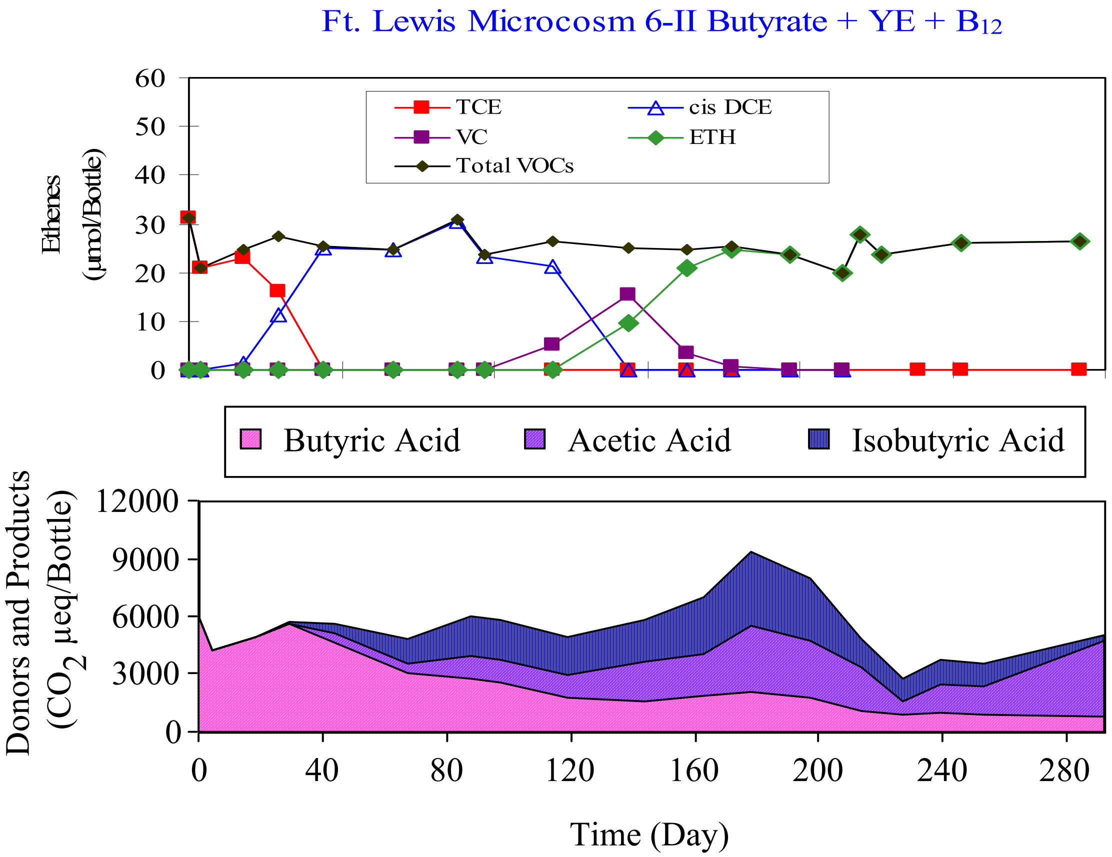
The depth to groundwater at the EGDY Site is approximately 10 feet bgs. Background groundwater velocities across the EGDY are in the range of 0.25 to 0.75 feet per day in the field test location. TCE, cDCE, VC, and BTEX constituents have been detected in groundwater samples from the EGDY Site. Of these, TCE and cDCE are most prevalent. Data from a previous investigation indicated that reductive dechlorination may be occurring in the area, but that the process is held up at cDCE.

B. Microcosms

Dechlorination in the Ft. Lewis microcosms was markedly slower than anticipated based on previous results with samples collected from Alameda Point and Cape Canaveral (Figure 5). The initial dose of TCE was removed from all of the amended, biotic reactors; however, formation of VC and complete conversion to ethene occurred in only a few bottles after 292 days of monitoring. The two amendments that did result in complete conversion to ethene in two of the three replicates were butyrate and high concentrations of yeast extract. Because the observed degradation of butyrate is slow, it appears to provide a relatively steady, long-term supply of electron equivalents for use.

The single, most important factor influencing dechlorination—both lag and extent—was probably the low native levels of TCE in the materials from which these microcosm sets were created. In the majority of bottles, there was a consistently long lag time observed prior to the initiation of cDCE dechlorination. However, once cDCE dechlorination activity began, it was generally followed by concurrent transformation of VC to ethene. These patterns suggest that the transformation of TCE was mediated by different organisms than those responsible for cDCE and VC dechlorination. This type of pattern is consistent with the presence of a dechlorinating population in which *Dehalococcoides ethenogenes* is not the dominant member.

Figure 5: Microcosm Results, Ft. Lewis, WA



C. Field Study

A conventional RABITT test system (shown in Figure 6.1 on page 54 of the draft RABITT protocol) was installed at Fort Lewis, with the exception that the gradient well was removed from the design based on the results of the tracer test and the measured gradient in the selected area. The three injection wells are spaced approximately 2 feet apart and the distances between the injection wells and each row of monitoring wells are 10 feet for a plot dimension of approximately 4 feet by 30 feet. A background monitoring well was installed upgradient of the plot to monitor any naturally occurring changes in background contaminant and geochemical profiles. An existing well in a contaminated area was used to provide the required supply of contaminated groundwater for injection into the test plot. The injected fluid imparts a gradient, which drives the flow of groundwater through the system.

Initial TCE concentrations across the test plot ranged from 11.0 to 47.9 µM (1,450 to 6,300 ppb). Injected groundwater initially contained moderately higher levels that tended to increase over the first 13 weeks of the demonstration from a low of 39.6 µM (5,200 ppb) at system startup to 148 µM (19,400 ppb) at 13 weeks. TCE concentrations remained within this range until Week 24 when concentrations spiked dramatically to 1,286 μM (169,000 ppb). Concerns that TCE levels of this magnitude would prove toxic to the microorganisms catalyzing the dechlorination reaction proved unwarranted as the conversion of TCE to cDCE continued unimpeded.

After 8 weeks of electron donor injection, the influent concentration of TCE was reduced 99.94% from 65 μM (8,500 ppb) to an average concentration of 0.04 μM (5 ppb) by the time it reached the first row of monitoring wells approximately 50 hours later. Assuming pseudo-first order kinetics apply, this rate of TCE removal translates into a half-life of 4.7 hours ($k = -0.1488\ h^{-1}$). This rate of removal remained constant when the influent concentration of TCE increased to 1,286 μM (169,000 ppb) during Week 24. The concentration in the injected water once it reached nearby MW-3 was only 0.53 μM (69.4 ppb), which translates into a half-life of 4.4 hours ($k = -0.155\ h^{-1}$).

The dramatic reduction in TCE concentrations contributed to the accumulation of cDCE during the demonstration. Increases in vinyl chloride levels suggest that cDCE was being dechlorinated, but at a significantly slower rate than TCE. The maximum VC concentration was only 3.5 μM (217 ppb) and comprised a very small percentage of the overall chloroethene mass. Ethene and ethane concentration remained at or near detection limits throughout most of the demonstration.

4.4 Site 4: Marine Corps Base Camp Lejeune, NC

A. Site Description

The contamination at Site 88, Marine Corps Base Camp Lejeune, occurred as a result of past operating procedures at the Base Dry Cleaners as well as due to leaking underground storage tanks at the site. The surficial aquifer was encountered at depths of 6 to 15 feet bgs. The aquifer consists of a series of sediments, primarily sand and clay, which commonly extend to depths of 75 feet. The principal water supply for the base is found in the series of sand and limestone beds that occur between 50 and 300 feet bgs. This series of sediments generally is known as the Castle Hayne Formation, associated with the Castle Hayne Aquifer. The top of the Castle Hayne Aquifer was found at a depth of 40 to 60 feet bgs. Clay layers occur in both of the aquifers. However, the layers are thin and discontinuous in most of the area, and no continuous clay layer separates the surficial aquifer from the Castle Hayne Aquifer. Thin, discontinuous layers and lenses of silt, clay, and/or peat are scattered throughout the sand. The hydraulic conductivity values estimated for the upper portion of the surficial aquifer ranged from 0.4 feet/day to 29.7 feet/day. The hydraulic conductivity values estimated for the lower portion of the surficial aquifer ranged from 56.4 feet/day to 85.5 feet/day.

B. Microcosms

Core samples were taken from Camp Lejeune for microbial analysis in November 2000. Because previous site characterization indicated varying contaminant and geochemical profiles at increasing depths, two distinct microcosm sets were constructed. The first set was assembled using core material and groundwater from 15 to 19 feet bgs, while the second used core material and groundwater from 45 to 49 feet bgs. The construction of two microcosm sets was undertaken to more fully assess the potential for stimulating dechlorinating activity in the area. Transferring material between two microcosms from different depths should provide information about potential inhibitory conditions at the site, as well as an indication of the promise of implementing a recirculating system in the field study. Monitoring of the Camp Lejeune microcosms is currently in-progress.

C. Field Study

A conventional RABITT test system consisting of 3 injection wells and an array of 9 monitoring wells was installed at Camp Lejeune in April 2001. The wells were installed to a depth of 48 ft bgs and covered an area approximately 4 ft wide by 30 ft long. Existing wells are being used to monitor background groundwater characteristics and supply groundwater for the demonstration. Injection of contaminated groundwater amended with butyric acid and yeast extract commenced in June 2001, with a total system pumping rate of approximately 0.65 L/min. The expected completion date for the field demonstration is December 2001.

Preliminary results show groundwater at the site is anaerobic, highly reduced (-200 mV), and PCE concentrations within the testing zone average about 33 μM (5,500 ppb). Other chloroethenes are present, but at considerably lower concentrations. The average concentrations of TCE, cDCE and VC within the testing zone are 2.9 μM, 0.8 μM, and <0.1 μM, respectively.

5. HEALTH AND SAFETY

Activities conducted during RABITT system installation and operation that could potentially cause health and safety hazards include drilling with hollow-stem augers or direct push methods, soil and groundwater sample collection, and replenishing concentrated stock solutions (tracer, nutrient, electron donor solutions). Potential hazards include exposure to organic contaminants and other chemicals used in stock solutions, exposure to organic vapors, objects striking feet or eyes, and electrical shock. Appropriate safety precautions and protective equipment is utilized to minimize or eliminate health and safety hazards.

6. ENVIRONMENTAL IMPACTS

Because the contaminants are biologically transformed in situ into non-hazardous compounds (e.g., ethene), the RABITT treatability test does not produce a process waste stream. Characterization and sampling activities generate a small amount of contaminated soil and groundwater that must be properly disposed.

7. COSTS

Detailed costs for all phases of the RABITT treatability approach will be presented in the final report.

8. CONCLUSIONS

To date RABITT demonstrations have been completed at three Department of Defense Facilities, Cape Canaveral Air Station, FL; Alameda Point, CA; and Ft. Lewis, WA. The fourth and final facility, Camp Lejeune, NC, has been initiated and will be completed by the end of the year.

Microcosm studies were conducted at each demonstration site to gauge the probability of enhancing reductive dechlorination and to examine a suite of electron donors for efficacy. In all four cases the electron donor butyric acid demonstrated results equal or superior to all other donors tested. This assessment is based on the percentage of reducing equivalents used for dechlorination and on the rate and degree of dechlorination.

The design and operation of each RABITT field demonstration system was tailored to site-specific characteristics. The site's hydrogeology, regulatory environment, and results from microcosm testing all influenced the design and operation of the system. An overview of each system's design is outlined in Table 2. Despite differences in site characteristics and system design, each of the three completed demonstrations showed rapid reduction of TCE to cDCE. At Cape Canaveral and Alameda this reduction proceeded to ethene. The demonstration at Ft. Lewis was exposed to extraordinarily high concentrations of TCE (169,000 ppb), but no slowdown in microbial activity was observed and dechlorination continued at a remarkable pace. The high-rate dechlorination observed at Ft. Lewis did lead to an accumulation of cDCE, but increases in the VC concentration suggest that dechlorination was proceeding past cDCE. Results from field demonstrations were generally in agreement with microcosm test results. Results from Camp Lejeune are still pending.

Table 2: Hydrogeology, Regulatory Environment and Results from Microcosm Testing

Design Parameter	Units	Cape Canaveral	Alameda Point	Ft. Lewis	Camp Lejeune
System flow rate	L/min	7.5	0.6	1.5	0.6
Flow pattern	NA	Circulation	Linear flow-through	Linear flow-through	Radial flow-through
Surface dimensions	ft.	10 x 34	3 x 15	4 x 30	4 x 30
Depth	ft. bgs	10-20	24-27	26-29	45-48
Sampling locations	number	49	12	12	12
Demonstration duration	Days	169	194	179	ongoing
Electron donor	NA	Lactic acid	Butyric acid	Butyric acid	Butyric acid
Yeast extract[a]	mg/L	None	20	20	20
Sodium bicarbonate[a]	mg/L	None	None	279	None

NA – not applicable.
a – target in situ concentration.

9. REFERENCES

1. DiStefano, T.D., J.M. Gossett, and S.H. Zinder. 1991. "Reductive Dechlorination of High Concentrations of Tetrachloroethene to Ethene by an Anaerobic Enrichment Culture in the Absence of Methanogenesis." *Applied and Environmental Microbiology* 57(8): 2287-2292.

2. DiStefano, T.D., J.M. Gossett, and S.H. Zinder. 1992. "Hydrogen as an Electron donor for Dechlorination of Tetrachloroethene by an Anaerobic Mixed Culture." *Applied and Environmental Microbiology* 58(11): 3622-3629.

3. Fennell, D.E., J.M. Gossett, and S.H. Zinder. 1997. "Comparison of Butyric Acid, Ethanol, Lactic Acid, and Propionic Acid as Hydrogen Donors for the Reductive Dechlorination of Tetrachloroethene." *Environmental Science & Technology* 31: 918-926.

4. Gossett, J.M., T.D. DiStefano, and M.A. Stover. 1994. *Biological Degradation of Tetrachloroethylene in Methanogenic Conditions*. U.S. Air Force Technical Report No. AL/EQ-TR-1983-0026, USAF Armstrong Laboratory, Environics Directorate, Tyndall AFB, FL.

5. Holliger, C., G. Schraa, A.J.M. Stams, and A.J.B. Zehnder. 1993. "A Highly Purified Enrichment Culture Couples the Reductive Dechlorination of Tetrachloroethene to Growth" *Applied and Environmental Microbiology* 59(9): 2991-2997.

6. Maymo-Gatell, X., V. Tandoi, J.M. Gossett, and S.H. Zinder. 1995. "Characterization of an H2-Utilizing Enrichment Culture that Reductively Dechlorinates Tetrachloroethene to Vinyl Chloride and Ethene in the Absence of Methanogenesis and Acetogenesis." *Applied and Environmental Microbiology* 61(11): 3928-3933.

7. Morse, J. J., B.C. Alleman, J.M. Gossett, S.H. Zinder, D.E. Fennell, G.W. Sewell, C.M. Vogel. 1998. *Draft Technical Protocol – A Treatability Test for Evaluating the Potential Applicability of the Reductive Anaerobic Biological In Situ Treatment Technology (RABITT) to Remediate Chloroethenes.* DoD Environmental Security Technology Certification Program. Document can be downloaded from www.estcp.org.

8. Smatlak, C.R., J.M. Gossett, and S.H. Zinder. 1996. "Comparative Kinetics of Hydrogen Utilization for Reductive Dechlorination of Tetrachloroethene and Methanogenesis in an Anaerobic Enrichment Culture." *Environmental Science and Technology* 30(9) 2850-2858.

Project No. 13

Permeable Reactive Barriers for In Situ Treatment of Chlorinated Solvents

Location	**Project Status**	**Media**	**Technology Type**
Dover Air Force Base, Delaware, USA	Final Report	Groundwater	*In situ* abiotic destruction of contaminants
Technical Contacts Charles Reeter U.S. Navy 1100 23rd Ave., Code 412 Port Hueneme, CA 93043 Tel: (805) 982-4991 Fax: (805) 982-4304 E-mail: reetercv@vfesc.navy.mil	**Project Dates** Accepted 1999 Final Report 2000	**Contaminants** Chlorinated solvents: PCE, TCE, and *cis*-1,2-DCE	
Catherine Vogel DoD SERDP/ESTCP Cleanup Program Manager 901 N. Stuart Street, Suite 303 Arlington, VA 22203 Tel: (703) 696-2118 Fax: (703) 696-2114 E-mail: vogelc@acq.osd.mil	**Costs Documented?** Yes	**Project Size** Field demonstration Pilot-scale	**Results Available?** Yes

Project 13 was completed in 2000.

1. INTRODUCTION

A permeable reactive barrier (PRB) was installed at Dover Air Force Base (AFB) in January 1998 to capture and treat a portion of a chlorinated solvent plume. The PRB consisted of a funnel-and-gate system with two permeable gates containing reactive media and impermeable funnel walls to achieve the required groundwater capture. This PRB was installed was installed to a depth of almost 40 ft using an innovative installation technique involving the use of caissons. The PRB was monitored periodically since installation and is performing satisfactorily in terms of contaminant degradation and groundwater capture (Battelle, 2000).

2. BACKGROUND

The Air Force Research Laboratory (AFRL), Tyndall Air Force Base (AFB), Florida contracted Battelle, Columbus, Ohio in April, 1997 to conduct a demonstration of a pilot-scale field PRB at Area 5, Dover AFB, Delaware. The Area 5 aquifer is contaminated with dissolved chlorinated solvents, primarily perchloroethene (PCE). The U.S. Department of Defense (DoD) Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technologies Certification Program (ESTCP) provided funding for this project. The primary objective of this demonstration was to test the performance of two different reactive media in the same aquifer, under uncontrolled field conditions. A secondary objective of the demonstration was to facilitate technology transfer through by documenting and disseminating the lessons learned regarding PRB design, construction, and monitoring.

The U.S. Environmental Protection Agency (EPA) National Exposure Research Laboratory (NERL) was funded separately by SERDP to conduct long-term above-ground column tests with groundwater from Area 5 of the Dover AFB to evaluate and select suitable pre-treatment and reactive cell treatment and media for the field demonstration. Members of the Remediation Technologies Development Forum

(RTDF) Permeable Barriers Group and the Interstate Technologies Regulatory Cooperation (ITRC) Permeable Barriers Subgroup provided document review support for this demonstration.

3. TECHNICAL CONCEPT

A PRB consists of permeable reactive media installed in the path of a contaminant plume. The natural groundwater flow through the permeable portion of the PRB brings the contaminants into contact with the reactive media. The contaminants are degraded upon contact with the media and treated groundwater emerges from the downgradient side of the PRB. Sometimes, impermeable "funnel" walls are installed next to the permeable "gate(s)" containing the media; the funnel helps to capture additional groundwater and channel it through the gate(s). A PRB design guidance document prepared by Battelle for AFRL describes the concept, design, construction, and installation of PRB systems in considerable detail (Gavaskar et al., 2000).

Based on column tests conducted with several alternative reactive media and Area 5 site groundwater, US EPA-NERL reported that a pyrite-and-iron combination ranked the best (U.S. EPA, 1997). Because of its potential for scrubbing oxygen and controlling pH in the iron-groundwater system, pyrite was expected to provide the benefits of enhanced kinetics of CVOC degradation and reduced precipitation of inorganic constituents. Precipitation of inorganic constituents, such as dissolved oxygen, carbonates, calcium, and magnesium, in the reactive medium is generally anticipated to be a probable cause for any loss of reactivity or hydraulic performance that the iron may encounter during long term operation. Precipitates could potentially coat the reactive surfaces of granular iron and reduce reactivity and hydraulic conductivity over time. Based on the U.S. EPA (1997) recommendation for the use of pyrite and iron to control precipitation, Battelle designed and installed a funnel-and-gate type PRB with two gates. Both gates have a reactive cell consisting of 100% granular iron. In addition, Gate 1 also incorporates a pre-treatment zone (PTZ) consisting of 10% iron and sand; Gate 2 incorporates a PTZ consisting of 10% pyrite and sand. The exit zone in both gates consists of 100% coarse sand. The construction of the PRB was completed in January 1998.

The location and design of the barrier was also determined by detailed Area 5 site characterization and modeling conducted in June 1997 to support the PRB and monitoring system design (Battelle, 1997). The groundwater treatment targets for this project are 5 µg./L of PCE and TCE, 70 µg/L of *cis*-1,2 dichloroethene (*cis*-1,2 DCE), and 2 µg/L of vinyl chloride (VC); these targets correspond to the U.S. EPA-recommended maximum contaminant levels (MCLs) for the respective chlorinated volatile organic compounds (CVOCs). An innovative construction technique involving caissons was used to install the two gates down to about 40 ft bgs, which is beyond the reach of conventional backhoe installation.

4. ANALYTICAL APPROACH

Following installation, the reactive (geochemical) and hydraulic performance of the PRB were evaluated primarily through two comprehensive monitoring events in July 1998 and June 1999 (Battelle, 2000a). Monitoring events were conducted periodically throughout the demonstration to monitor a limited number of operating parameters. At the end of 18 months of operation, core samples of the gate and surrounding aquifer media were collected and analyzed for precipitate formation.

5. RESULTS

Monitoring results show that, to date, the PRB is functioning at an acceptable level in terms of capturing groundwater, creating strongly reducing conditions, and achieving treatment targets. The treatment targets at Dover AFB are 5 µg/L of PCE and TCE, 70 µg/L of *cis* 1,2-dichloroethene (DCE), and 2 µg/L of vinyl chloride (VC); DCE and VC are typical byproducts of PCE and TCE degradation process. The PTZs in both gates succeeded in removing dissolved oxygen from the groundwater before it entered the reactive cell. In addition, the use of pyrite did result in some degree of pH control while the groundwater was in the PTZ of Gate 2. However, once the groundwater entered the reactive cell, the tendency of the iron to raise the pH of the system overwhelmed any pH control effect achieved by the pyrite. Magnesium, nitrate, and silica were the main inorganic species precipitating out of the low-alkalinity groundwater as it flowed through the gates.

6. HEALTH AND SAFETY

A health and safety plan was prepared before construction started and was reviewed by Dover AFB and all contractors. A pre-construction meeting was held at the site to discuss safety issues. Level D safety measures and personal protective equipment (PPE) were used to address the minimal safety hazards during construction. These consisted of a hard-hat and steel-toed shoes for workers at the site. When the vibratory hammer was used to drive the caissons into the ground, workers used earplugs to protect potential hearing loss. Entry of workers into the excavation was avoided by using a pre-fabricated frame holding the monitoring well array that was inserted from the ground into the excavated gates. The granular iron was placed in the gates with a tremie tube. No health and safety incidents occurred during construction.

7. ENVIRONMENTAL IMPACTS

A photo-ionization detector was used to monitor ambient organic vapors during construction. Because of the very low levels of organic contaminants present in the groundwater and soil at the location of the PRB, there were no real concerns about environmental impacts. Extracted soil from the caisson was transported to a nearby construction site for reuse.

8. COSTS

The initial capital investment incurred the pilot-scale PRB at Dover AFB Area 5 was a total of US$739,000, including US$47,000 for the granular iron media and US$264,000 for the on-site construction; site characterization, column testing, design, site preparation, and procurement accounted for the rest of the cost. A long-term life cycle analysis of a full-scale PRB (expanded funnel-and-gate system with four gates) and an equivalent pump-and-treat (P&T) system was conducted for the site. Assuming that the iron medium would sustain its reactivity and hydraulic properties for at least 30 years, the discounted net present value (NPV) of the long-term savings over 30 years of operation was estimated to be approximately US$800,000, compared with using the P&T system. Given that the solvent plume is likely to last for several decades or even centuries, the longer-term savings are significant.

9. CONCLUSIONS

A pilot-scale PRB was successfully designed and installed at Dover AFB to capture and treat a chlorinated solvent plume to meet the desired clean up targets. The caisson method of installation was found to be suitable for installing a PRB at relatively greater depths and in the midst of underground utility lines. Monitoring shows that the PRB continues to meet its targets. One significant unknown is the longevity of the PRB, that is, for how long will the iron medium continue to sustain it reactive and hydraulic performance. Precipitates were found to be forming in the iron cell due to the level of inorganic constituents measured in the groundwater. In the absence of longevity information, the cost analysis described above was repeated assuming that the iron would have to be replaced every 5, 10, 20, or 30 years. This economic analysis showed that as long as the iron does not have to be replaced for at least 10 years, the PRB would be a less costly option compared to an equivalent P&T system at Area 5. Dover AFB is currently considering an expansion of the system to capture more of the plume.

10. REFERENCES AND BIBLIOGRAPHY

1. Battelle, 2000. *Design, Construction, and Monitoring of the Permeable Reactive Barrier in Area 5 at Dover Air Force Base*. Final report prepared for the Air Force Research Laboratory by Battelle, Columbus, Ohio, USA on March 31, 2000.

2. Battelle, 1997. *Design/Test Plan: Permeable Barrier Demonstration at Area 5, Dover AFB*. Prepared for Air Force Research Laboratory by Battelle, Columbus, Ohio.

3. Gavaskar, A., N. Gupta, B. Sass, R. Janosy, and J. Hicks. *Design Guidance for the Application of Permeable Reactive Barriers for Groundwater Remediation*. Prepared for Air Force Research Laboratory by Battelle, Columbus, Ohio on March 31, 2000.

4. U.S. EPA, 1997. *Selection of Media for the Dover AFB Field Demonstration of Permeable Barriers to Treat Groundwater Contaminated with Chlorinated Solvents*. Preliminary report to U.S. Air Force for SERDP Project 107. August 4, 1997.

Project No. 14

Thermal Cleanup Using Dynamic Underground Stripping and Hydrous Pyrolysis/Oxidation

<table>
<tr><td>Location
LLNL Gasoline Spill Site, Livermore, CA.

Visalia Pole Yard, Visalia, CA.</td><td>Project Status
Final Report</td><td>Contaminants
PAHs, diesel and pentachlorophenol (Visalia)
Gasoline (LLNL)
(TCE, solvents and fuels at other sites)</td><td>Technology Type
Dynamic underground stripping and hydrous pyrolysis/ oxidation</td></tr>
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Fax: 301-903-3877
E-mail: paul.beam@em.doe.gov</td><td>Project Dates
Accepted 1998
Final Report 1999</td><td colspan="2">Media
Groundwater and soil</td></tr>
<tr><td>Costs Documented?
Yes</td><td>Project Size
Full-scale:

Livermore: 100,000yd^3 (76,000 m^3)

Visalia: 4.3 acres, >130 ft deep (app. 600,000 m^3)</td><td>Results Available?
Yes</td></tr>
</table>

Project 14 was completed in 1999.

1. INTRODUCTION

In the early 1990s, in collaboration with the School of Engineering at the University of California, Berkeley, Lawrence Livermore National Laboratory developed dynamic underground stripping (DUS), a method for treating subsurface contaminants with heat that is much faster and more effective than traditional treatment methods. More recently, Livermore scientists developed hydrous pyrolysis/oxidation (HPO), which introduces both heat and oxygen to the subsurface to convert contaminants in the ground to such benign products as carbon dioxide, chloride ion, and water. This process has effectively destroyed all contaminants it encountered in laboratory tests.

With dynamic underground stripping, the contaminants are vaporized and vacuumed out of the ground, leaving them still to be destroyed elsewhere. Hydrous pyrolysis/oxidation technology takes the cleanup process one step further by eliminating the treatment, handling, and disposal requirements and destroying the contamination in the ground. When used in combination, HPO is especially useful in the final "polishing" of a site containing significant free-product contaminant, once the majority of the contaminant has been removed.

2. BACKGROUND

A. Lawrence Livermore National Laboratory (LLNL) Gasoline Spill Site:

LLNL recently completed the cleanup and closure of a moderate-sized spill site in which thermal cleanup methods, and the associated control technologies, were used to remediate nearly 8,000 gallons (30,000 L) of gasoline trapped in soil both above and below the standing water table. The spill originated from a group of underground tanks, from which an estimated 17,000 gallons (64,000 L) of gasoline leaked sometime between 1952 and 1979. The gasoline penetrated the soil, eventually reaching the water table, where it spread out. Gasoline trapped up to 30 ft (9 m) below the water table was there due to a rise in the water table after the spill occurred, with the gasoline held below water by capillary forces in the soil. Groundwater contamination extended about 650 ft (200 m) beyond the central spill area. The soils at the site are alluvial, ranging from very fine silt/clay layers to extremely coarse gravels, with unit permeabilities ranging over several orders of magnitude. The site was prepared for long-term groundwater pump-and-treat with vapor extraction; recovery rates prior to thermal treatment were about 2.5 gal/day 9.5 L/day).

B. Visalia Pole Yard:

In 1997, DUS and HPO were applied for cleanup of a 4.3 acre (17,000 m^2) site in Visalia, California, owned by Southern California Edison Co. (Edison). The utility company had used the site since the 1920s to treat utility poles by dipping them into creosote, a pentachlorophenol compound, or both. By the 1970s, it was estimated that 40-80,000 gallons (150,000-300,000 L) of DNAPL product composed of pole-treating chemicals (primarily creosote and pentachlorophenol) and an oil-based carrier fluid had penetrated the subsurface to depths of approximately 100 ft (30 m), 40 ft (12 m) below the water table. Edison had been conducting pump and treat operations at the site for nearly 20 years. While this activity had successfully reduced the size of the offsite groundwater contaminant plume, it was not very effective at removing the NAPL source. Prior to thermal treatment, about 10 lb. (4.5 kg) of contaminant was being recovered per week. Bioremediation of the free-organic liquids is expected be prohibitively slow (enhanced bioremediation was predicted to take at least 120 years).

3. TECHNICAL CONCEPT

A. Dynamic Underground Stripping (DUS): Mobilization and Recovery

Dynamic Underground Stripping combines two methods to heat the soil, vaporizing trapped contaminants. Permeable layers (e.g., gravels) are amenable to heating by steam injection, and impermeable layers (e.g., clays) can be heated by electric current. These complementary heating techniques are extremely effective for heating heterogeneous soils; in more uniform conditions, only one or the other may be applied. Once vaporized, the contaminants are removed by vacuum extraction. These processes - from the heating of the soil to the removal of the contaminated vapor - are monitored and guided by underground imaging, which assures effective treatment through *in situ* process control.

B. Hydrous Pyrolysis/Oxidation (HPO): In Situ Destruction

At temperatures achieved by steam injection, organic compounds will readily oxidize over periods of days to weeks. By introducing both heat and oxygen, this process has effectively destroyed all petroleum and solvent contaminants that have been tested in the laboratory. All that is required is for water, heat, oxygen, and the contaminant to be together; hence the name. After the free organic liquids are gone, this oxidation will continue to remove low-level contamination. The oxidation of contaminants at steam temperatures is extremely rapid (less than one week for TCE and two weeks for naphthalene) if sufficient oxygen is present. In HPO, the dense, nonaqueous-phase liquids and dissolved contaminants are destroyed in place without surface treatment, thereby improving the rate and efficiency of remediation by rendering the hazardous materials benign by a completely *in situ* process. Because the subsurface is heated during the process, HPO takes advantage of the large increase in mass transfer rates, such as increased diffusion out of silty sediments, making contaminants more available for destruction.

C. Underground Imaging: process control

Most subsurface environmental restoration processes cannot be observed while operating. Electrical Resistance Tomography (ERT) has proven to be an excellent technique for obtaining near-real-time images of the heated zones. ERT gives the operator detailed subsurface views of the hot and cold zones at their site on a daily basis. Heating soil produces such a large change in its electrical properties that it is possible to obtain images between wells (inverted from low voltage electrical impulses passed between) of the actual heated volumes by methods similar to CAT scans. Combined with temperature measurements, ERT provides process control to ensure that all the soil is treated.

D. LLNL Gasoline Spill Site: DUS

The DUS application at the LLNL Gasoline Spill Site was designed to remove free-product NAPL. The targeted volume was a cylinder about 120 ft (36 m) in diameter and 80 ft (24 m) high, extending from a depth of 60 ft (18 m) to a depth of 140 ft (43 m). The water table is located at 100 ft (30 m). Due to the presence of relatively thick clay-rich zones, both electrical heating and steam injection were required to heat the target volume.

E. Visalia Pole Yard: DUS + HPO

Thermal treatment (DUS steam injection and vacuum extraction) was chosen for removal of the free product contaminant. The overall objectives of thermal remediation of the Visalia Pole Yard are to remove a substantial portion of the DNAPL contaminant at the site, thereby enhancing the bioremediation of remaining contaminant. This is expected to significantly shorten the time to site closure as well as improve the accuracy of the prediction of time to closure. As part of the final removal process, Edison is also implementing hydrous pyrolysis (HPO), an *in situ* method of destroying organic contaminants using small amounts of supplemental air or oxygen. The primary use of HPO at this site is for destruction of residual pentachlorophenol, which will not readily steam strip due to high solubility and low vapor pressure. The combination of rapid recovery and thermal destruction is expected to permit Edison to achieve their cleanup goals, which included termination of groundwater treatment.

A series of noble gas tracer tests were conducted to verify the extent of HPO under field conditions. Evidence of hydrous pyrolysis/oxidation came from the disappearance of dissolved oxygen, the appearance of oxidized intermediate products, the production of CO_2, and the distinct isotopic signature of the carbon in the CO_2 produced, indicating contaminant origin. These results constrain the destruction rates throughout the site, and enable site management to make accurate estimates of total *in situ* destruction based on the recovered carbon using the system-wide contaminant tracking system being used on the site.

4. ANALYTICAL APPROACH

Standard laboratory analyses were performed on all samples unless noted specifically in the references.

5. RESULTS

A. LLNL Gasoline Spill Site:

During 21 weeks of thermal treatment operations conducted over about a year, DUS treatment removed more than 7600 gallons (29,000 L) of an estimated 6200 gallons (23,000 L) of gasoline trapped in soil both above and below the water table. Prior to thermal treatment, separate phase contamination extended to >120 ft (37 m) deep. Approximately 100,000 yd^3 (76,000 m^3) were cleaned. The maximum removal rate was 250 gallons (950 L) of gasoline a day. The process was limited only by the ability to treat the contaminated fluids and vapors on the surface.

Dynamic underground stripping removed contaminants 50 times faster than with the conventional pump-and-treat process. The cleanup, estimated to take 30 to 60 years with pump-and-treat, was completed in about one year. As of 1996, following removal of more than 99% of the contaminant, and achievement of Maximum Contaminant Limit (MCL) levels in groundwater for five of the six contaminants, the site is being passively monitored under an agreement with the California Regional Water Quality Control Board (RWQCB), California EPA's Department of Toxic Substances Control (DTSC), and the Federal EPA Region 9. These regulatory agencies declared that no further remedial action is required.

The initial objective of the LLNL DUS demonstration was to remove the separate phase gasoline from the treatment area. Not only was the separate phase gasoline removed, but the groundwater contamination was reduced to or near the regulatory limits. Thermal treatment under these conditions did not sterilize the site, and instead led to the establishment of flourishing indigenous microbial ecosystems at soil temperatures up to 90˚C. The very positive response of regulators, who provided quick closure authorization for the site, indicates that these methods will be accepted for use.

B. Visalia Pole Yard:

During the first six weeks of thermal remediation operations, between June and August 1997, approximately 300,000 pounds (135 metric tons) of contaminant was either removed or destroyed in place, a rate of about 46,000 pounds (22 metric tons) per week. That figure contrasts sharply with the 10 pounds (0.003 metric ton) per week that Edison had been removing with conventional pump and treat cleanup methods. In fact, the amount of hydrocarbons removed or destroyed in place in those six weeks was equivalent to 600 years of pump-and-treat, about 5,000 times the previous removal rate.

Edison achieved their initial goal of heating over 500,000 yd^3 (380,000 m^3) to at least a temperature of 100 ^oC by the beginning of August 1997. Uniform heating of both aquifer and aquitard materials was achieved. At this point, about 20,000 gallons (76,000 L) of free-product liquid had been removed. Vapor and water streams continued to be saturated with product. Continued destruction by HPO was indicated by high levels of carbon dioxide (0.08 - 0.12% by volume) removed through vapor extraction. Initial destruction accounted for about 300 lb/day 136 kg/day) of contaminant being destroyed via HPO. Operations were changed to a huff and puff mode, where steam is injected for about a week, and then injection ceases for about a week while extraction continues. Maximum contaminant removal is obtained during this steam-off period as the formation fluids flash to steam under an applied vacuum.

In September, 1997, following the initial contaminant removal by steam injection and vacuum extraction, air was injected along with the steam to enhance hydrous pyrolysis of the remaining contaminant. *In situ* destruction rates increased to about 800 lb/day (360 kg/day). Recovery/destruction rates matched expectations. By the summer of 1998, decreasing contaminant concentrations indicated that the bulk of the contaminant had been removed from the main treatment volume. Groundwater concentrations indicated that the site was being cleaned from the periphery inward, with all but two wells showing contaminant concentrations similar to the pre-steam values by September 1998. Active thermal remediation of this zone was nearing completion. At this point, Edison chose to begin injecting steam into a deeper aquifer to heat and remove the remaining contamination that had leaked into the overlying silty aquitard, which represented the "floor" of the initial treatment zone. Contaminant is being recovered from this aquitard today.

In the ensuing months, recovery rates have remained high. As of March 1999, over 960,000 lb (440,000 kg) or 116,000 gallons of contaminant had been removed or destroyed. About 18% of the total has been destroyed in situ via HPO. Contaminant concentrations in the recovery wells are decreasing.

Edison plans to continue steam injection through the end of June 1999. This will be followed by groundwater pumping, vacuum extraction and air injection to enhance HPO and bioremediation. Monitoring of groundwater concentrations is expected to continue for a period of 2 to 5 years.

6. HEALTH AND SAFETY

This high-energy system needs to be handled in accordance with standard safety procedures. Monitoring of air emissions has revealed low emissions with no worker safety or public health impacts.

7. ENVIRONMENTAL IMPACTS

Permits were required for water discharge (treated effluent) and NO_x emissions from the boilers. The site is being remediated under a state-lead Remedial Action Plan (RAP). Vapor is destroyed in the boilers under air permit from the regional air board. Standard regional groundwater monitoring is conducted to ensure public health protection.

8. COSTS

A. DUS at the LLNL Gasoline Spill Site

The first application of dynamic underground stripping at the Livermore gasoline spill site in 1993 cost about $110 per cubic yard ($140 per cubic meter); removing the additional research and development costs suggested the project could have been repeated for about $65 per cubic yard ($85 per cubic meter). The alternatives would have been significantly higher. Because contamination at the gasoline spill at the Livermore site had migrated downward over 130 ft (40 meters), digging up the contaminated soil and disposing of it would have cost almost $300 per cubic yard ($400 per cubic meter). Soil removal and disposal costs are more typically in the range of $100 to $200 per cubic yard ($130 to $260 per cubic meter); pump-and-treat method costs are as high as or higher than soil removal costs.

B. DUS and HPO at the Visalia Pole Yard

Use of DUS and HPO in combination can permit huge cost savings because HPO eliminates the need for long-term use of expensive pump and treat treatment facilities by converting some contaminants to benign products in situ and mobilizing other contaminants. Site operators can adjust process time to enhance removal DUS or in situ destruction through HPO. Because the treatment is simple, it can be readily applied to large volumes of earth.

Edison has projected the life-cycle cost of steam remediation at the Visalia pole yard to be under $20 million, which includes all construction, operation and monitoring activities. The total treatment zone includes about 800,000 yd^3 (600,000 m^3) of which about 400,000 yd^3 (300,000 m^3) contained DNAPL contamination. Approximately $4.2 million was spent on capital engineering, design, construction, and startup. In addition, about $12 million had been spent on operations, maintenance, energy (gas and electric), monitoring, management, engineering support, and regulatory interface by the end of 1998. Since Edison (the site owner) has acted as primary site operator for the cleanup, the aforementioned project costs do not reflect a profit in the overhead costs. Post-steaming operations will consist of the operation of the water treatment system for an expected duration of two to five years to demonstrate compliance with the California State EPA Remediation Standards. The annual operations and maintenance costs for the water treatment plant is $1.2 million. The previously-approved cleanup plan of pump and treat with enhanced bioremediation was expected to cost $45 million (in 1997 US dollars) for the first 30 years; it was expected to take over 120 years to complete the cleanup.

The Visalia pole yard cleanup is the only commercial application of this method to date, but indications are that large-scale cleanups with hydrous pyrolysis/oxidation may cost less than $25 per cubic yard ($\$33/m^3$), an enormous savings over current methods. Perhaps the most attractive aspect of these technologies is that the end product of a DUS/HPO cleanup with bioremediation as a final step is expected to be a truly clean site.

9. CONCLUSIONS

Breakthrough cleanups of seemingly intractable contaminants are now possible using a combined set of thermal remediation and monitoring technologies. This “toolbox” of methods provides a rapid means to clean up free organic liquids in the deep subsurface. Previously regarded as uncleanable, contamination of this type can now be removed in a period of 1-2 years for a cost less than the many-decade site monitoring and pumping methods it replaces. The groundwater polishing by HPO provides the means to completely clean serious NAPL-contaminated sites.

The gasoline spill demonstration clearly showed that thermal methods can quickly and effectively clean a contaminated site. With respect to the Visalia Pole Yard cleanup, tremendous removal rates have been achieved. More than 970,000 lb. of contaminants was removed or destroyed in about 20 months of operations; previous recovery amounted to 10 lb/week. Contaminant concentrations are dropping in the extraction wells; the site is cleaning from the periphery inward. Site management plans to terminate active thermal treatment soon, returning to pumping and monitoring the site. The expectations are that groundwater treatment will no longer be necessary after a few years.

The Visalia field tests confirmed *in situ* HPO destruction in soil and ground water at rates similar to those observed in the laboratory, under realistic field remediation conditions. HPO appears to work as fast as oxygen can be supplied, at rates similar to those measured in the laboratory. The predictive models used to design HPO steam injection systems have been validated by using conservative tracers to confirm mixing rates, oxygen consumption, CO_2 release, and effects of real-world heterogeneity. Accurate field measurements of the critical fluid parameters (destruction chemistry, oxygen content, steam front location) were demonstrated, using existing monitoring wells and portable data systems with minimal capital cost.

Several sites are designing DUS/HPO applications similar to Visalia. These include both solvent and pole-treating chemical contaminated sites, ranging in depth from relatively shallow (<40 ft (10 m)) to relatively deep (>185 ft (56 m)). In January 1999, steam injection began at a relatively shallow (>35 ft (11 m)) site in Ohio in which DNAPL TCE is being removed.

10. REFERENCES AND BIBLIOGRAPHY

1. Aines, R.D.; Leif, F.; Knauss, K.; Newmark, R.L.; Chiarappa, M.; Davison, M.L.; Hudson, G.B., Weidner, R.; and Eaker, C.; Tracking inorganic carbon compounds to quantify in situ oxidation of polycyclic aromatic hydrocarbons during the Visalia Pole Yard hydrous pyrolysis/oxidation field test, 1998 (in prep).

2. Cummings, Mark A.; Visalia Steam Remediation Project: Case Study of an Integrated Approach to DNAPL Remediation. *Los Alamos National Laboratory Report, LA-UR-9704999; 1997; 9 pp.*

3. Knauss, Kevin G.; Aines, Roger D.; Dibley, Michael J.; Leif, Roald N.; Mew, Daniel *A.;* Hydrous Pyrolysis/Oxidation: In-Ground Thermal Destruction of Organic Contaminants. *Lawrence Livermore National Laboratory, Report, UCRL-JC 126636, 1997; 18 pp.*

4. *Knauss, Kevin G.; Dibley, Michael J.; Leif, Roald N.; Mew, Daniel A.; Aines, Roger D. "Aqueous Oxidation of Trichloroethene (TCE): A Kinetic and Thermodynamic Analysis". In* Physical, Chemical and Thermal Technologies, Remediation of Chlorinated and Recalcitrant Compounds, Proceeding of the First International Conference on Remediation of Chlorinated and Recalcitrant Compounds; *Wickramanayake, G.B., Hinchee, R.E., Eds.; Battelle Press, Columbus, OH, 1998a; pp359-364. Also available* as Lawrence Livermore National Laboratory, Report, UCRL-JC-129932*, 1998; 8 pp.*

5. *Knauss, Kevin G.; Dibley, Michael J.; Leif, Roald N.; Mew, Daniel A.; Aines, Roger D. "Aqueous Oxidation of Trichloroethene (TCE): A Kinetic analysis." Accepted for Publication,* Applied Geochemistry*; 1998b.*

6. *Knauss, Kevin G.; Dibley, Michael J.; Leif, Roald N.; Mew, Daniel A.; Aines, Roger D. "Aqueous Oxidation of Trichloroethene (TCE) and Tetrachloroethene (PCE) as a Function of Temperature and Calculated Thermodynamic Quantities, Submitted to* Applied Geochemistry*; 1998c.*

7. *Leif, Roald N.; Chiarrappa, Marina; Aines, Roger D.; Newmark Robin L.; and Knauss, Kevin G. "In Situ Hydrothermal Oxidative Destruction of DNAPLS in a Creosote Contaminated Site." In* Physical, Chemical and Thermal Technologies, Remediation of Chlorinated and Recalcitrant Compounds, Proceeding of the First International Conference on Remediation of Chlorinated and Recalcitrant Compounds; *Wickramanayake, G.B., Hinchee, R.E., Eds.; Battelle Press, Columbus, OH, 1998; pp 133-138. Also available as Lawrence Livermore National Laboratory, Report,* UCRL-JC-129933*, 1998a; 8 pp.*

8. *Leif, Roald N.; Knauss, Kevin G.; and Aines, Roger D.; Hydrothermal Oxidative Destruction of Creosote and Naphthalene,* Lawrence Livermore National Laboratory, Report, UCRL-JC*, 1998b 21 pp (in prep).*

9. *Leif, Roald N.; Aines, Roger D.; Knauss, Kevin G. Hydrous Pyrolysis of Pole Treating Chemicals: A) Initial Measurement of Hydrous Pyrolysis Rates for Naphthalene and Pentachlorophenol; B) Solubility of Flourene at Temperatures Up To 150°C;* Lawrence Livermore National Laboratory, Report, UCRL-CR-129938*, 1997a; 32pp.*

10. *Leif, Roald N.; Knauss, Kevin G.; Mew, Daniel A.; Aines, Roger D. Destruction of 2,2',3-Trichlorobiphenyl in Aqueous Solution by Hydrous Pyrolysis / Oxidation (HPO).* Lawrence Livermore National Laboratory, Report, UCRL-ID 129837*, 1997b; 21 pp.*

11. MSE Technology Applications, Inc., "Dynamic Underground Stripping and Hydrous Pyrolysis/Oxidation Cost Analysis", *report prepared for the U.S. Department of Energy, HMP-44,* June, 1998.

12. Newmark, R.L., ed., Dynamic Underground Stripping Project: LLNL Gasoline Spill Demonstration Report; *Lawrence Livermore National Laboratory, Report UCRL - ID - 116964*, July, 1994 (1600 pages).

13. Newmark, Robin L.; Aines, Roger D.; Dumping Pump and Treat: Rapid Cleanups Using Thermal Technology. *Lawrence Livermore National Laboratory, Report, UCRL-JC 126637*, 1997; 23 pp.

14. Newmark, R.L., R. D. Aines, G. B. Hudson, R. Leif, M. Chiarappa, C. Carrigan, J. Nitao, A. Elsholz, C. Eaker, R. Weidner and S. Sciarotta, *In Situ* destruction of contaminants via hydrous pyrolysis/ oxidation: Visalia field test, *Lawrence Livermore National Laboratory, Report UCRL-ID-132671*, 1998; 45 pp.

15. Newmark, R.L., R. D. Aines, G. B. Hudson, R. Leif, M. Chiarappa, C. Carrigan, J. Nitao, A. Elsholz, and C. Eaker, 1999. An integrated approach to monitoring a field test of in situ contaminant destruction*, Symposium on the Application of Geophysics to Engineering and Environmental Problems* (SAGEEP) '99, Oakland, CA, March 15-18, 1999, 527-540.

16. Ramirez, A.L., W. D. Daily and R. L. Newmark, Electrical resistance tomography for steam injection monitoring and process control, *Journal of Environmental and Engineering Geophysics,* (July, 1995), v. 0, no.1, 39-52.

17. Udell, K and McCarter, R (1996) Treatability Tests of Steam Enhanced Extraction for the Removal of Wood Treatment Chemicals from Visalia Pole Yard Soils, University of California, Report to Southern California Edison. (<http://abacus.me.berkelley.edu/BERC/Projects/Visalia/index.html>)

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Phytoremediation of Chlorinated Solvents</td></tr>
<tr><td>Location
Aberdeen Proving Grounds, Edgewood Area J-Field Site, Edgewood, MD

Edward Sears Site,
New Gretna, NJ

Carswell Air Force Base,
Fort Worth, TX</td><td>Project Status
Final Report</td><td>Media
Groundwater</td><td>Technology Type
Phytoremediation</td></tr>
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E-mail: Gregory.Harvey@wpafb.af.mil</td><td>Project Dates
Accepted 1998</td><td colspan="2">Contaminants
Chlorinated solvents: TCE, 1,1,2,2-TCA, PCE, and DCE</td></tr>
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Full-scale field demonstration</td><td>Results Available?
Yes (preliminary)</td></tr>
<tr><td colspan="3">Project Reports
Available upon completion of projects. When available, these reports can be obtained from the National Service Center for Environmental Publications (NCEPI), P.O. Box 42419, Cincinnati, OH 42542-8695; tel: (800) 490-9198, or (513) 489-8695.</td></tr>
</table>

Project 15 was completed in 1999.

1. INTRODUCTION

The efficacy and cost of phytoremediation to clean up shallow groundwater contaminated with chlorinated solvents (primarily trichloroethylene), is being evaluated at the field scale in demonstration projects at Aberdeen Proving Grounds Edgewood Area J-Field Site in Edgewood, Maryland, the Edward Sears site in New Gretna, New Jersey, and Carswell Air Force Base in Fort Worth, Texas. These projects will demonstrate the use of hybrid poplars to hydraulically control the sites and ultimately to remove the volatile organic compounds (VOCs) from the groundwater. When completed, these projects will allow a comparison of phytoremediation at three sites under varied conditions within different climatic regions.

2. SUMMARY AND LATEST OBSERVATIONS

At the Aberdeen Proving Ground site, a process called deep rooting is being used to achieve hydraulic influence. Hybrid poplar trees were initially planted in the spring of 1996 at five to six feet below ground surface to maximize groundwater uptake. The field demonstration and evaluation will be for a five year period. The U.S. Geological Survey has estimated that hydraulic influence will occur when 7,000 gallons of water per day are removed from the site.

Several trees were excavated in the fall of 1998 to determine root growth. The tree roots were found to be confined to the hole in which they were placed. In an attempt to increase root depth and width, new trees were planted in holes of varying sizes and depths.

The latest field data indicates that hydraulic influence is occurring. Current tree uptake is 1,091 gallons (4,129 liters) per day and is expected to increase to 1,999 gallons (7,528 liters) at the end of 30 years. Contaminant uptake is minimal at this time but is expected to improve as the trees mature. Groundwater sampling indicates that the contaminated plume has not migrated off-site during the growing season and sampling data showed non-detectable emissions from transpiration gas. There are several on-going studies to determine if deleterious compounds retained in the leaves and soil could pose risks to environmental receptors.

At the Edward Sears site, deep rooting was also used to maximize groundwater uptake. Beginning in December 1996, hybrid poplar trees were planted nine feet below ground surface. In addition, some trees were planted along the boundary of the site at depth of only 3 feet to minimize groundwater and rainwater infiltration from off-site. Groundwater monitoring will continue in 2000. A November sampling is scheduled to determine if contaminant concentrations recover during the dormant season.

There were substantial reductions in dichloromethane and trimethylbenzene concentrations during the 1998 growing season. For example, dichloromethane was reduced to 615 parts per billion (ppb) from 490,000 ppb at one location and to a non-detect level from up to 12,000 ppb at another location; trimethylbenzene was reduced to 50 ppb from 1,900 at one location. There is also indication of anaerobic dechlorination in the root zone as the level of PCE dropped and TCE increased.

There seems to have been an adverse impact on tree growth in areas with high VOCs concentrations during the initial two growing seasons. However, in the third growing season, the rate of growth has increased significantly but the trees have yet to achieve the height and diameter of trees planted in uncontaminated areas. Evapotranspiration gasses were collected in sampling bags during the hottest periods of the day and were analyzed for target compounds. Only low levels of toluene (8 to 11 ppb) were detected. Soil gas flux measurements indicated that no contaminants are released into the air from the soil.

At the Carswell Air Force Base site, the phytoremediation system is a low-cost, low-maintenance system that is consistent with a long-term contaminant reduction strategy. Trees were planted in trenches as a short rotation woody crop employing standard techniques developed by the U.S. Department of Energy. The phytoremediation system was designed to intercept and remediate a chlorinated ethene contaminant plume. The system relies on two mechanisms to achieve this goal: hydraulic removal of contaminated groundwater through tree transpiration and biologically mediated in-situ reductive dechlorination of the contaminant. The tree root systems introduce organic matter into the aquifer system, which drives the microbial communities in the aquifer from aerobic to anaerobic communities that support this reductive dechlorination.

The first three growing seasons resulted in a remediation system that reduced the mass of contaminants moving through the site. The maximum observed reduction in the mass flux of TCE across the downgradient end of the site during the three-year demonstration period was 11 percent. Increases in hydraulic influence and reductive dechlorination of the dissolved TCE plume are expected in out years, and may significantly reduce the mass of contaminants. Modeling results indicate that hydraulic influence alone may reduce the volume of contaminated groundwater that moves offsite by up to 30 percent. The decrease in mass flux that can be attributed to *in situ* reductive dechlorination has yet to be quantified.

3. SITE DESCRIPTION

Aberdeen Proving Grounds, Maryland

The site is located at the tip of the Gunpowder Neck Peninsula, which extends into the Chesapeake Bay. The Army practiced open trench (toxic pits) burning/detonation of munitions containing chemical agents and dunnage from the 1940s to the 1970s. Large quantities of decontaminating agents containing solvents were used during the operation. The surficial groundwater table had been contaminated with solvents (1,1,2,2-TCA, TCE, DCE) at levels up to 260 parts per million (ppm). The contamination is 5 to 40 ft (3.5 to 13 m) below ground surface. The plume is slow-moving due to tight soils and silty sand. The impacted area is a floating mat-type fresh water marsh approximately 500 ft (160 m) southeast. A low environmental threat is presented by the contaminant plume.

Edward Sears Site, New Jersey

From the mid-1960s to the early 1990s, Edward Sears repackaged and sold expired paints, adhesives, paint thinners, and various military surplus materials out of his backyard in New Gretna, NJ. As a result, toxic materials were stored in leaky drums and containers on his property for many years. The soil and groundwater were contaminated with numerous hazardous wastes, including dichloromethane (up to 490,000 ppb), tetrachloroethylene (up to 160 ppb), trichloroethylene (up to 390 ppb), trimethylbenzene (up to 2,000 ppb), and xylenes (up to 2,700 ppb). There is a highly permeable sand layer from 0 to 5 ft (0 to 1.6 m) below ground surface (bgs). Below that exists a much less permeable layer of sand, silt, and clay from 5 to 18 (1.6 to 6 m) ft bgs. This silt, sand, and clay layer acts as a semi-confining unit for water and contaminants percolating down toward an unconfined aquifer from 18 to 80 ft (6 to 26 m) bgs. This unconfined aquifer is composed primarily of sand and is highly permeable. The top of the aquifer is about 9 ft (3 m) bgs, which lies in the less permeable sand, silt, and clay layer. The top of the aquifer is relatively shallow and most of the contamination is confined from 5 to 18 ft 1.6 to 6 m) bgs.

Carswell AFB, Texas

The U.S. Air Force Plant 4 (AFP4) and adjacent Naval Air Station, Fort Worth, Texas, has sustained contamination in an alluvial aquifer through the use of chlorinated solvents in the manufacture and assembly of military aircraft. Dispersion and transport of TCE and its degradation products have occurred, creating a plume of contaminated groundwater. This project is led by the U.S. Air Force (USAF) and is being conducted as part of the Department of Defense's (DOD's) Environmental Security Technology Certification Program (ESTCP), as well as the U.S. Environmental Protection Agency's (U.S. EPA's) Superfund Innovative Technology Evaluation (SITE) Program. Planting and cultivation of Eastern Cottonwood (*Populus deltoides*) trees above a dissolved TCE plume in a shallow (under 12 ft) aerobic aquifer took place in spring 1996. The trees were planted as a short rotation woody crop employing standard techniques developed by the U.S. Department of Energy (DOE) to grow biomass for energy and fiber. Data are being collected to determine the ability of the trees to perform as a natural pump-and-treat system.

4. DESCRIPTION OF THE PROCESS

Aberdeen Proving Grounds, Maryland

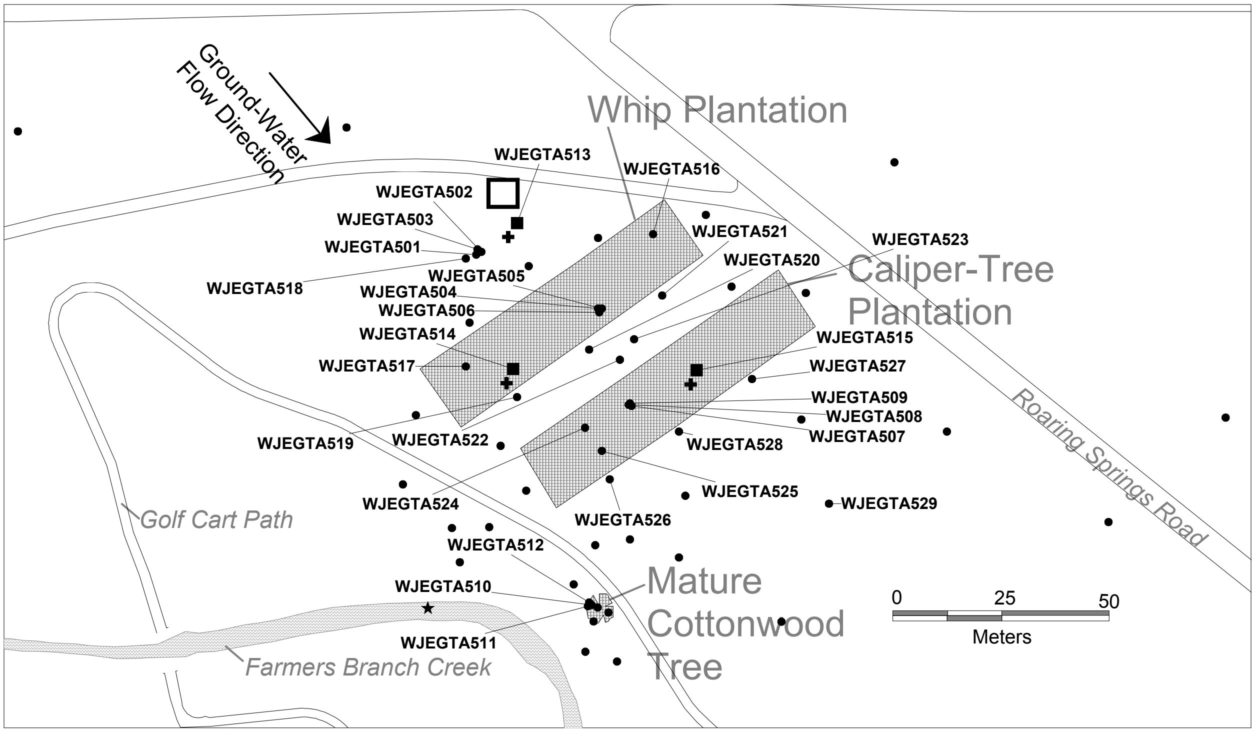
Phytoremediation was selected to provide both hydraulic influence of the groundwater plume and mass removal of contaminants.

The plantation area being monitored is approximately 2034 m^2 and contains 156 viable poplars. 1,1,2,2-TCA and TCE are 90 percent of the contaminants (total approximately 260 ppm solvents). USGS estimated 7000 gals/day removal would achieve hydraulic influence. The duration of evaluation will be five years.

Process Description —
After agronomic assessment, two-year-old hybrid poplar 510 trees were planted 5 to 6 ft (1.6 to 2 m) deep in the spring of 1996. Surficial drainage system was installed to remove precipitation quickly and allowed trees to reach groundwater.

Various sampling methods were employed during the 1998 growing season to determine if project objectives are being met. The methodologies, which yielded the most valuable data include: groundwater sampling; sap flow monitoring; tree transpiration gas and condensate sampling; and exposure pathway assessments. In addition to field sampling activities, new trees were planted on the site in October 1998 to increase the phytoremediation area and assess the usefulness of native species for phytoremediation.

Figure 1: Aberdeen Proving Grounds, Maryland



EXPLANATION

• MONITORING WELL: Well number indicates well was sampled throughout the entire location

□ STREAM-STAGE GAGE

□ TENSIOMETER NEST

Ó MONITORING WELL WITH WATER-LEVEL RECORDER

□ WEATHER STATION

Edward Sears Site, New Jersey

In December 1996, 118 hybrid poplar saplings (*Populus charkowiiensis x incrassata*, NE 308) were planted in a plot approximately one-third of an acre in size.

Poplar trees that were left over after the deep rooting was completed were planted to a depth of 3 ft (1 m), or shallow rooted. These trees were planted along the boundary of the site to the north, west, and east sides of the site. These trees will minimize groundwater and rainwater infiltration from off-site.

Process Description—
The trees were planted 10 ft (3 m) apart on the axis running from north to south and 12.5 ft (4 m) apart on the east-west axis. The trees were planted using a process called deep rooting: 12-ft (4 m) trees were buried nine feet under the ground so that only about 2 to 3 ft (0.6 to 1 m) remained on the surface. This was done to enhance deep rooting of poplar trees in the zone of contamination, and to maximize uptake of groundwater compared to surface water.

Monitoring of the site includes semi-annual analysis of groundwater, soils, soil gas, and evapotranspiration gas. Continued growth measurements will also be made as the trees mature. Site maintenance also involves fertilization, and control of insects, deer and unwanted vegetation.

Carswell AFB, Texas

This demonstration investigated eastern cottonwood trees planted as a short rotation woody crop to help remediate shallow aerobic TCE-contaminated groundwater in a subhumid climate.
The study determined the ability of the planted system to hydraulically control the migration of contaminated groundwater, as well as biologically enhance the subsurface environment to optimize *in situ* reductive dechlorination of the chlorinated ethenes.

In addition to investigating changes in groundwater hydrology and chemistry, the trees were studied to determine important physiological processes such as rates of water usage, translocation and volatilization of volatile compounds, and biological transformations of chlorinated ethenes within the plant organs. Since planted systems may require many years to reach their full remediation potential, the study also made use of transpiration and hydrologic predictive models to extrapolate findings to later years.
A mature cottonwood tree (about 20 years old) and section of the underlying aquifer located proximal to the study area were investigated to provide evidence of transpiration rates and geochemical conditions that eventually may be achieved at the site of the planted trees.

This project was evaluated for its ability to reduce the mass of TCE that is transported across the downgradient end of the site (mass flux). The following performance objectives were established: (1) there would be a 30 percent reduction in the mass of TCE in the aquifer that is transported across the downgradient end of the site during the second growing season, as compared to baseline TCE mass flux calculations; and (2) there would be a 50 percent reduction in the mass of TCE in the aquifer that is transported across the downgradient end of the site during the third growing season, as compared to baseline TCE mass flux calculations. To evaluate the primary claim, groundwater levels were monitored and samples were collected and analyzed for TCE concentrations over the course of the study.
Secondary objectives were addressed to help understand the processes that affect the downgradient migration of TCE in the contaminated aquifer at the site, as well as to identify scale-up issues. These secondary objectives include: determine tree growth rates and root biomass; analyze tree transpiration rates to determine current and future water usage; analyze the hydrologic effects of tree transpiration on the contaminated aquifer; analyze contaminant uptake into plant organ systems; evaluate geochemical indices of subsurface oxidation-reduction processes; evaluate microbial contributions to reductive dechlorination; collect data to determine implementation and operation costs for the technology; and determine plant enzyme levels for various mature trees in the local area.

Process description —
In April 1996, the U.S. Air Force planted 660 eastern cottonwoods in a one acre area. The species *P. deltoides* was chosen over a hybridized species of poplar because it is indigenous to the region and has therefore proven its ability to withstand the Texas climate, local pathogens, and other localized variables that may affect tree growth and health.

Two sizes of trees were planted: whips and 5-gallon (20 L) buckets. The 5-gallon bucket trees are expected to have higher evapotranspiration rates due to their larger leaf mass.

Site managers plan to increase monitoring at the site to include a whole suite of water, soil, air, and tree tissue sample analysis. Some of the more unique data colleted (in relation to the other case study sites) are analyses of microbial populations and assays of TCE degrading enzymes in the trees.

5. RESULTS AND EVALUATION

Aberdeen Proving Grounds, Maryland

1. Examination of groundwater level data revealed an area of depression within the poplar plantation indicating that hydraulic influence is occurring. Currently, the trees are removing approximately 1,091 gallons per day (4,129 L/day) and at the end of 30 years are expected to remove approximately 1,999 gallons per day (7,528 L/day).
2. Groundwater sampling indicated that the contaminated plume has not migrated off-site during the growing seasons.
3. There are no ecological impacts that are attributable to the plantation area. Sampling data have shown non-detectable off-site migration of emissions from transpiration gas.
4. Peak transpiration is estimated to occur in approximately 10 to 15 years.
5. Limitations include depth of contamination, but there are no limitations for concentrations of up to 260 ppm for solvents. Weather and growing season are the most influential factors.
6. Contaminant uptake is minimal at this time but is expected to improve as the trees mature.
7. A groundwater model is under development to quantify the degree of containment generated by the trees. The model requires an accurate estimate of water withdrawal rates by the trees to determine if phytoremediation will work as a remedial alternative for the site.
8. This demonstration project is on-going and will be further evaluated for efficacy and costs.

Groundwater samples and elevations were collected, seasonally from the on-site wells to determine VOC concentrations and if trees were facilitating hydraulic influence of the plume. Results indicated that an area of drawdown exists within the tree zone during the spring and summer when tree transpiration is the greatest. In 1998, additional wells were installed using a Geoprobe® in order to more accurately assess VOC concentrations and groundwater elevation. A groundwater model is currently being developed to predict potential VOC removal by the trees and when complete hydraulic influence may be attained. Given the success of the groundwater sampling, the sampling objectives for 1999 included groundwater elevation monitoring and sampling and a continued effort to refine the groundwater model.

Sap flow monitoring was performed to determine the amount of water being removed by individual trees. In order to increase monitoring accuracy, new sap flow probes were purchased which are placed directly into the tree tissue as opposed to resting on the trunk of the tree. Comparison of new equipment with previous methods indicates that the new methodology provides an even more accurate estimation of net transpiration rate with less data interference or “noise.” Future sampling objectives for the site include continued seasonal sap flow monitoring for the purposes of estimating transpiration rates.

Seasonal tree transpiration gas and condensate sampling continued in the 1998 sampling season to assess the release of VOCs from the trees. Previous methods consisted of placing a 100-liter Tedlar® bag over a section of branch and then sampling the gas and any condensate trapped within the bag. This method was modified in 1998 with the addition of a cold trap which would potentially remove excess moisture from the bag and keep the leaves in a more ambient temperature. Comparison of the two methods, with and without cold trap, indicates that the cold trap apparatus may not be powerful enough to sufficiently cool the temperature within the bag. Future transpiration gas monitoring was planned for the 1999 sampling season with the addition of a modified cold trap attachment.

Several studies were designed which examined exposure pathways. Leaves and soil were collected from the phytoremediation area and a reference area for a leaf degradation study. The study is designed to determine whether or not there are deleterious compounds retained within the study leaves or within the associated soil which could pose risk to an environmental receptor. The results of this study are still being analyzed. Additional studies involved nematode analyses which examined the trophic assemblage of the nematode community. Data collected in 1997 indicated that the nematode community was enhanced in the phytoremediation area as compared with data collected prior to the tree planting.

No trees were planted in the 1999 sampling season. The objectives were: 1) to assess the phytoremediation capabilities of native Maryland species, tulip trees and silver maples, in addition to hybrid poplar trees; 2) to increase the area of hydraulic influence; 3) to diversify the age of trees to ensure continued containment and contaminant removal; and 4) to assess new planting methods. The last objective relates to the three tree excavations performed in the fall of 1998. Three trees were excavated and replanted in their same areas on the site to examine root depth and structure and whether or not the trees were utilizing groundwater. Examinations revealed that most tree roots appeared to be confined to the hole in which they were placed and did not appear to radiate extensively from this area. It did appear however, that the tree roots were deep enough to access the groundwater. Three new planting methods (i.e., hole sizes and widths) were employed for the new trees in an attempt to provide the tree roots with either increased depth, increased width or a combination of increased width and depth. Monitoring of these new trees during the 1999 sampling season attempted to discern the phytoremediation capabilities of the native species versus the hybrid poplars and to assess the growth of the new trees given the various planting methods employed for each.

Edward Sears Site, New Jersey

Over 40 direct push microwells were installed to monitor groundwater instead of temporary direct push wells. This will enabled frequent, seasonal monitoring of groundwater, at specific locations for comparable costs.

Substantial reductions in dichloromethane identified after the second growing season in August 1998 have been sustained as of August 1999. Concentrations at four locations were reduced from 490,000 down to 615 ppb, 12,000 ppb to ND, 680 ppb to ND, and 420 to 1.2 ppb. At one location PCE dropped from 100 to 56 ppb, while TCE increased from 9 to 35 ppb. This may be indicative of anaerobic dechlorination in the root zone. At other locations TCE concentrations remained stable over the past three years, although a decrease from 99 to 42 ppb was noted at one well point. Trimethylbenzene (TMB) was reduced from 147 to 2 ppb, 246 to ND, 1900 to 50 ppb, and 8 to 1 ppb at four microwell points in the treated area. At another well point within the treated area, concentrations of TMB were relatively unaffected, 102 ppb in August 1997 compared to 128 in August 1999. Xylenes were also unaffected or slightly increased at this same location, 26 ppb in August 1997 compared to 34 ppb in August 1999. At two other locations, xylene concentrations dropped from 590 to 17 ppb, and from 56 to 1.4 ppb.
The groundwater monitoring program will continue in 2000, with samples being collected in May, August and November. November sampling is being added to see if concentrations recover slightly during the dormant season.

Sampling of evapotranspiration gases was conducted by placing Tedlar bags over branches on 6 selected trees. Five trees were in areas where groundwater was contaminated with different concentrations of target contaminants. The sixth tree was in an area known to be free of contamination. Evapotranspiration gasses were collected on an hourly basis, for four hours during the hottest period of the day. Low levels of toluene 8 to 11 ppb were detected in three of four samples from one tree and one of four discrete gas samples from another tree. No other target compounds were detected (DL of 8 ppb/v) in any other samples.

Soil gas flux measurements were collected in conjunction with the evapotranspiration gas study. Samples collected indicated no contaminants being released to the air from the soils.

During the initial two growing seasons, tree height and diameter were substantially lower in areas containing high concentrations of VOCs in groundwater. This adverse impact appears to have been reduced during the third (1999) growing season. Rate of growth increased significantly in the contaminated areas, however these trees have yet to achieve the overall height and diameter of trees planted in uncontaminated areas. Overall the trees in August 1998 averaged 17 ft (22 m) in height with a range from 3.5 to 25 ft (1 to 8 m).

Carswell AFB, Texas

Root biomass and extent were examined in September of 1997 in the whip and caliper-tree plantations. Four trees from each plantation were evaluated for fine root biomass and length, coarse root biomass. Coarse root mass was significantly greater in the caliper trees in the 3.0 to 10 mm range; 458 g per tree compared to 240 g per tree. Although the coarse root mass in the > 10 mm range was also greater in the caliper trees than in the whips, the difference was not statistically significant. Differences in the fine root biomass between the plantations were not statistically significant: 288 g/m^2 for whips compared to 273 g/m^2 for caliper trees in the <0.5 mm range; 30 g/m^2 for whips compared to 36 g/m^2 for the caliper trees in the 0.5 to 1.0 mm range; and 60 g/m^2 for the whips compared to 91 g/m^2 for the caliper trees in the 1.0 to 3.0 mm range. Fine root length density in the upper 30 cm of soil was statistically greater in the caliper trees as compared.

In the second growing season (September 1997), the roots of both the whips and caliper trees had reached the water table (275 cm for the whips and 225 cm for the caliper trees), and the depth distribution of the roots was quite similar. The more expensive planting costs of the caliper trees did not appear to impart any substantial benefit with regard to root depth and biomass. Observed differences between the whips and the caliper trees were reported to be due as much to inherent genotypic differences as to the different modes of establishment.

The trees in both the whip and caliper-tree plantations at the demonstration site began to use water from the aquifer and measurably decrease the volumetric flux of contaminated groundwater leaving the site during the period of demonstration. The maximum reduction in the outflow of contaminated groundwater that could be attributed to the trees was approximately 12 percent and was observed at the peak of the third growing season. The reduction in the mass flux of TCE across the downgradient end of the treatment system at this time was closer to 11 percent because TCE concentrations were slightly higher during the third growing season than at baseline. The maximum observed drawdown of the water table occurred near the center of the treatment system at this time and was approximately 10 centimeters. A groundwater flow model (MODFLOW) developed by the USGS indicates that the volume of water that was transpired from the aquifer during the peak of the third growing season was probably closer to 20 percent of the initial volume of water that flowed through the site because there was an increase in groundwater inflow to the site due to an increase in the hydraulic gradient on the upgradient side of the drawdown cone.

Tree-growth and root-growth data collected from the demonstration site are consistent with the observations of hydraulic influence of the trees on the contaminated aquifer. Trees in the whip plantation, which were planted approximately 1.25 m apart, were starting to approach canopy closure by the end of the third growing season. This observation indicates that the trees were transpiring a significant amount of water at this time. (A plantation approaches its maximum transpiration potential once it achieves a closed canopy because a closed canopy limits leaf area.)

The caliper trees were planted 2.5 m apart and although the plantation was not as close to achieving a closed canopy, individual caliper trees transpired just over twice the water that individual whips transpired. As a result, the volume of water that was transpired by the two plantations was similar because there were only half as many caliper trees as whips.

The physiologically based model PROSPER, which was used to predict out-year transpiration rates at the demonstration site, indicates that there will be little difference in the amount of water that the whip and caliper tree plantations will transpire. Transpiration for each plantation is predicted to range from 25 to 48 cm per growing season depending on climatic conditions, soil moisture, and root growth. Forty-eight to fifty-eight percent of this predicted evapotranspiration is predicted to be derived from the contaminated aquifer (saturated zone) regardless of the plantation.

Since the phytoremediation system had not achieved maximum hydraulic control during the period of demonstration, the groundwater flow model was used to make predictions with regards to out-year hydraulic control. The groundwater flow model indicates that once the tree plantations have achieved a closed canopy, the reduction in the volumetric flux of contaminated groundwater across the downgradient end of the site will likely be between 20 and 30 percent of the initial amount of water that flowed through the site. The actual amount of water that will be transpired from the aquifer by the tree plantations will be closer to 50 to 90 percent of the volume of water that initially flowed through the site. The discrepancy between the reduction in the volumetric outflow of groundwater and the volume of water transpired from the aquifer can be attributed to the predicted increase in groundwater inflow to the site and the release of water from storage in the aquifer. No hydraulic control was observed during the dormant season from November to March for the demonstration site.

The amount of hydraulic control that can be achieved by phytoremediation is a function of site-specific aquifer conditions. A planted system can be expected to have a greater hydrologic affect on an aquifer at a site that has an initially low volumetric flux of groundwater than at a site where the flux of contaminated groundwater is significantly greater. The parameters of hydraulic conductivity, hydraulic gradient, saturated thickness, and aquifer width in the treatment zone all contribute to the volumetric flux of groundwater through a site. The horizontal hydraulic conductivity at the demonstration site in Fort Worth, Texas is approximately 6 m/day. The natural hydraulic gradient is close to two percent and the saturated thickness of the aquifer is between 0.5 and 1.5 m. Volume of water in storage in an aquifer will also affect system performance.

When designing for hydraulic control during phytoremediation, it is important to keep the remediation goals in mind. In other words, it may not be desirable to achieve full hydraulic control at a site if full control would adversely affect the groundwater/surface-water system downgradient of the site. At the demonstration site in Texas, the receptor is Farmers Branch Creek, which has very low flow (less than 1 ft^3/sec or 3 cm^3/s) during the summer months (period of peak transpiration). The optimal performance at such a site may be to keep the plume from discharging into the creek without drying up the creek, particularly since hydraulic control is only one mechanism that contributes to the cleanup of a groundwater plume by phytoremediation. A groundwater flow model of a potential site is ideal for addressing such design concerns.

With respect to the fate of the contaminants that were taken up into the planted trees, TCE and its daughter products were commonly detected in tissue samples of roots, stems and leaves. Generally, there was an increase over time in the percentage of planted trees in which the compounds were detected. Stem tissue generally exhibited the greatest diversity and concentration of chlorinated compounds. A research team investigated the kinetics of transformation of TCE for leaf samples collected from seven trees (cedar, hackberry, oak, willow, mesquite, cottonwood whip, cottonwood caliper tree). Each of the plant species investigated appears to have properties that are effective in degrading TCE. Specifically, all leaf samples showed dehalogenase activity. Pseudo first-order rate constants were determined for the samples. The average and standard deviation for all seven rate constants is 0.049 ± 0.02 per hour. This corresponds to a half life of 14.1 hours. These kinetics are fast relative to other environmental transport and transformation processes with the exception of volatilization for TCE. As a result, it is unlikely that degradation within the trees will be the rate limiting step during phytoremediation. These data suggest that it may better to use species that are native to a proposed site rather than genetically altered plants that are designed to enhance metabolism of TCE.

With respect to biologically induced reductive dechlorination, there is evidence that the aquifer beneath the planted trees was beginning to support anaerobic microbial communities capable of biodegradation of TCE within three years of planting. Specifically, microbial data from soil and groundwater samples indicate that the microbial community beneath the planted trees had begun to move towards an assemblage capable of supporting reductive dechlorination during the demonstration period. In addition, dissolved oxygen concentrations had decreased and total iron concentrations had increased at the southern end of the whip plantation where the water table is closest to land surface. The ratio of TCE to *cis*-1,2-DCE had also decreased at this location beneath the whip plantation, which suggests that the shift toward anaerobic conditions in this part of the aquifer was beginning to support the biodegradation of TCE. Significant contaminant reduction by this mechanism, however, had not occurred across the demonstration site by the end of the demonstration period.

Data from the aquifer beneath a mature cottonwood tree near the planted site support the conclusion that reductive dechlorination can occur beneath cottonwood trees with established root systems. The ratio of TCE to *cis*-1,2-DCE beneath the mature tree was typically one order of magnitude less than elsewhere at the site during the demonstration. The microbial population in the area of the mature cottonwood tree included a vibrant community that supported both hydrogen oxidizing and acetate fermenting methanogens. This active anaerobic population is assumed to be responsible for the decrease in TCE concentration and the generation of daughter products beneath the mature cottonwood tree.

Preliminary field data collected during the fifth dormant season (January 2001) indicate that the trees were finally beginning to have a widespread effect on the geochemistry of the ground water. During this season, dissolved oxygen concentrations were above 4.5 mg/L in water from all upgradient wells and one well between the tree plantations (well 522). Whereas, they were below 3.5 mg/L in water from all other wells at the demonstration site, including wells that are over 50 m downgradient of the planted area. The mean dissolved oxygen concentration in water from all wells, excluding the upgradient wells and well 522, was 1.76 mg/L. The dissolved oxygen concentration in several wells beneath the planted trees was less than 1 mg/L. In addition, preliminary field data indicate that ferrous iron and/or sulfide concentrations were elevated in several locations beneath and immediately downgradient of the tree plantations. These data add to the body of evidence that the planted trees at the demonstration site can stimulate microbial activity that results in the depletion of dissolved oxygen in the aquifer and the creation of local anaerobic conditions conducive to microbial reductive dechlorination (Eberts, et al., In press). These data also support the conclusion that the ground-water system was still in a state of transition after 5 years. Hansen (1993) reports that soil carbon is significantly related (positive) to tree age and that there is a net addition of soil carbon from plantations older than about 6 to 12 years of age. Even though reductive dechlorination has been observed around the mature tree, the presence of TCE daughter products, as well as residual TCE, indicate that the reductive dechlorination process has not fully mineralized the contaminants of concern to innocuous compounds. There is no field evidence from this study that suggest complete *in situ* biodegradation of TCE and its daughter products can be achieved.

6. COSTS

Aberdeen Proving Grounds, Maryland

Site Preparation (?):	$5,000
Capital:	$80,000 for UXO clearance of soil during planting; $80/tree.

Operation and maintenance: $30,000 due to no established monitoring techniques

Edward Sears Site, New Jersey

Site Preparation: $24,000
Planting: $65,700
Maintenance: $15,300
Total: $105,000
1997 Maintenance: $26,000
1998 Maintenance: $14,000 (Maintenance cost will drop substantially after trees are established)

Monitoring/analysis: 50 groundwater stations, soil gas, soils, hydrogeological parameters, weather, transpiration gas, reports, etc. Monitoring costs should also reduce annually as study techniques become more refined.

1997: $72,800
1998: $61,600
1999: $42,000

Carswell AFB, Texas

Preparatory Work
Site Characterization: $12,000
Site Design: $10,000
Site Work:
Monitoring (research level) well installation: $90,000
Development of Plantations –1 acre (includes landscaping costs): $41,000
Weather Station: $3,100
Survey: $25,000
Purchase of Trees
Whips ($0.20 each): $100
Five-gallon buckets ($18 each): $2,000

Installation of Irrigation System: $10,000
Yearly O&M:
Landscaping: $2,000
Groundwater, soil, vegetation, transpiration, climate, soil moisture, and water-level monitoring (research level): $250,000

The planting costs at Carswell are significantly less than proprietary planting techniques employed by the vendors that involve auguring down to the capillary fringe and other engineered methods for individual tree planting.

After Treatment: None

7. REFERENCE

Eberts, S., G. Harvey, S. Jones, and S. Beckman, In press. *A Multiple Process Assessment of Phtoremediation of a Chlorinated Solvent Plume at a Subhumid Field Site*, John Wiley and Sons.

Project No. 16 **In-Situ Heavy Metal Bioprecipitation**			
Location Industrial site in Belgium	**Project Status** Final	**Contaminants** Heavy metals (zinc, cadmium, arsenic, lead, chromium, nickel, copper), sulphate	**Technology Type** *In-situ* bioremediation (reactive zone or biobarrier)
Technical Contact Dr. Ludo Diels Dr. Leen Bastiaens Ir Karolien Vanbroekhoven Flemish Institute for Technological Research (Vito) Boeretang 200 B-2400 Mol Belgium Tel: +32 14 33 51 00 Fax: +32 14 58 05 23	**Project Dates** Accepted 1999 Final report 2002	**Media** Groundwater	
	Costs Documented? No	**Project Size** Laboratory, Pilot/full-scale	**Results Available?** Yes

1. INTRODUCTION

The industrial world is facing many problems concerning soils and groundwater with heavy metal pollution. This pollution is mainly due to mining activities and non-ferrous activities by e.g. the metal refining, metal processing, and surface treatment industries. Immobilization followed by fytostabilization has been shown to be effective for treating polluted soil in order to reduce the risk of heavy metals being spread around by wind erosion or leaching from the soil into the groundwater (Van der Lelie et al., 1998). But what about groundwater that has already been contaminated with heavy metals?

When dealing with dissolved inorganic contaminants, such as heavy metals, the required process sequence in a ‘pump & treat’ system to remove the dissolved heavy metals present in the groundwater becomes very complex and costly. In addition, the disposal of the metallic sludge, in most cases as a hazardous waste, is also very cost prohibitive. Therefore, *in situ* treatment methods capable of achieving the same mass removal reactions for dissolved contaminants in an *in situ* environment are evolving and gradually gaining prominence in the remediation industry.

In this project a relatively innovative technique will be studied for *in situ* treatment of groundwater containing heavy metals. Through stimulation of sulphate reducing bacteria (SRBs) in aquifers and groundwater heavy metals can be bioprecipitated, hereby reducing the risk of further spreading of the metals. The feasibility of this technique will be evaluated for 2 different industrial sites in Belgium. In-situ bioprecipitation of heavy metals can be implemented as a biological reactive zone or biowall. The concept of *in situ* reactive zones is based on the creation of a subsurface zone where migrating contaminants are intercepted and permanently immobilised into harmless end products.

2. SITE DESCRIPTION

On industrial **site 1** (metal smelter) high concentrations of zinc (10-150 mg/l), cadmium (0.4-4 mg/l) and arsenic (20-270 µg/l) are present in the groundwater. Also relatively high concentrations of sulphate (400-700 mg/l) were measured, which is favourable for SRB-activities. Groundwater samples taken further away from the source have lower metals and sulphate concentrations.

Industrial **site 2** (surface treatment) has serious chromium (up to 8300 µg/l), zinc (up to 78 mg/l), lead (up to 72 µg/l), nickel (up to 3500 µg/l), copper (92 mg/l) and cadmium (up to 17 mg/l) problems in the groundwater. Very high sulphate (up to 3000 mg/l) concentrations are also present. This groundwater has also a very low pH (between 2 and 4).

Industrial **site 3** (landfill) has a serious As (up to 1,200 µg As/l) and Zn (up to 880 µg Zn/l) in the leachate. Also high sulphate (up to 3,800 mg/l) concentrations are present. The pH was between 2.6 and 6.0.

3. DESCRIPTION OF THE PROCESS

Bioprecipitation Process:

In-situ precipitation of heavy metals and sulphates is a method based on stimulation of SRBs by supplementing an appropriate electron donor. Addition of extra nutrients (N and P) might also be required for good growth of the bacteria. In the presence of a suitable electron donor (for instance acetate) SRBs reduce sulphates to sulphites and further to sulphides, which then form stable and rather insoluble metal sulphides:

$$\mathbf{CH_3COOH + SO_4^{2-} \Longrightarrow 2\ HCO_3^- + HS^- + H^+}$$

$$\mathbf{H_2S + Me^{++} \Longrightarrow \underline{MeS}\ + 2\ H^+}$$

A good *in situ* bioprecipitation process however can only be obtained under the following conditions:

- Sulphate reducing bacteria (SRBs) must be present in the aquifer. In case no SRBs are present among the autochthonous micro-population in the aquifer, appropriate micro-organisms have to be introduced in the aquifer.
- Sulphate should be available at a sufficiently high concentration.
- Also nutrients and an appropriate electron donor such as methanol, ethanol, molasses, acetate or lactate are required.
- No oxygen should be present and a low redox potential (E_h) is necessary.

The applicability of *in-situ* bioprecipitation of heavy metals on sites should therefor be evaluated case by case.

Outline of the Project:

1. Preliminary study
    - Site evaluation
2. Lab-scale treatability testing in batch and column experiments
    - The presence of SRBs in the aquifers will be examined by microbial countings, measurements of SRB-activity and PCR-technology.
    - Selection of a suitable organic substrate
    - Determination of optimal physico-chemical conditions: required concentration of the electron donor, nutrients requirement, sulphate requirements, influence of temperature, …
    - As the effectiveness of a reactive zone is determined largely by the relationship between the kinetics of the target reactions and the rate at which the mass flux of contaminants passes through it with the moving groundwater, kinetics of metal removal from groundwater will be examined.
    - The stability of the formed metal sulphides will be checked.
    - Further is clogging due to biomass production and metal precipitates an important issue that has to be evaluated.
3. Field demo on pilot or full scale
4. Monitoring

4. RESULTS/COSTS

The first preliminary studies and site investigations were done. Afterwards groundwater and (undisturbed) aquifer material samples were taken and investigated in batch systems under different conditions in order to follow redox potential and the reduction of the dissolved metals. Special attention was paid to the isolation of SRBs and the identification with special probes (study under way). In the project acetate was chosen as carbon source (no explosion danger like methanol, not contaminated by other impurities like molasse). Different concentrations of acetate were added and the SRB *Desulfovibrio desulfuricans* Dd8301 was added as a positive control. The results for the removal of Zn at the first site are presented in Table 1. It can be concluded that without addition of a carbon source or by inhibiting the bacterial activity (addition of $HgCl_2$) nearly no Zn removal could be obtained. The addition of a low concentration of acetate lead to a reduction of Zn from 10700 µg Zn/l to 213 µg Zn/l. In the same groundwater As and Cd were also removed and precipitated. The addition of too high concentrations of acetate did not lead to metal removal because the methanogenic bacteria dominated the scene (very high gas production was observed). The addition of a specific SRB could in some cases only reduce the lag time of the bacterial growth. In the last condition no groundwater was used and only aquifer in water. It was observed that some metals from the aquifer material were solubilised and afterwards precipitated by the added *Desulfovibrio desulfuricans* Dd8301. Metals were removed only in those conditions where the redox potential was below –220 mV.

At site 1 the metal removal of a lower contaminated groundwater (further away from the source) was evaluated too. The sulphate concentrations were also quite low and this showed to be not favourable for the SRB-bacteria. Only in the case of added SRBs the metals could be removed.

Table 1: Zn Removal by In-situ Bioprecipitation Under Different Conditions for site 1

	T0		T4		T8		T12	
	Total	In solution	Total	In solution	Total	In solution	Total	In solution
aquifer + groundwater	100,000	101,000	82,100	87,600	80,900	79,200	67,300	62,600
aquifer + groundwater + 0.5 mM $HgCl_2$	107,000	109,000	98,000	104,000	97,800	94,200	76,800	73,200
aquifer + groundwater + 1 ml K-acetate (25%)	107,000	109,000	96,100	99,600	85,500	82,800	**213**	**101**
aquifer + grondwater + 5 ml K-acetate (25%)	101,000	103,000	103,000	102,000	112,000	109,000	101,000	96,100
aquifer + grondwater + 1 ml K-acetate (25%) + Dd8301	94,500	93,100	82,600	86,500	77,500	77,200	62,400	59,000
aquifer + grondwater + 5 ml K-acetate (25%) + Dd8301	96,000	96,100	92,800	95,300	105,000	91,600	88,200	86,000
aquifer + Postgate C medium + Dd8301	1680	885	**1570**	**334**	**50**	**10**	**57**	**41**

At the second test site the sulphate concentrations were quite low (200 mg SO_4^{2-}/l). Only after the addition of extra sulphate (2000 mg SO_4^{2-}/l) or of zero valent iron the redox could be reduced to below –200 mV. The redox conditions are presented in table 2. Table 3 shows the removal of Ni from the groundwater by bioprecipitation. The above mentioned conditions lead to complete Ni removal. Note that the conditions without carbon source or with inhibition of the bacterial activity (addition of $HgCl_2$) did not lead to metal removal. Also Pb, Zn, Cr and Cd could be removed.

Table 2: Redox Potential Under Different Conditions for Groundwater from test site 2

Test conditions	T0	T1	T4	T8	T12	T19
R1: aquifer + GW	197 mV	201 mV	203 mV	181 mV	235 mV	247 mV
R2: aquifer + GW + $HgCl_2$	325 mV	316 mV	341 mV	309 mV	315 mV	301 mV
R3: aquifer + GW + K-acetate	175 mV	173 mV	132 mV	159 mV	198 mV	143 mV
R4: aquifer + GW + K-acetate + Dd8301	229 mV	197 mV	290 mV	250 mV	145 mV	142 mV
R5: aquifer + GW + Postgate C + K-acetate + Dd8301	88 mV	44 mV	-308 mV	-322 mV	-284 mV	-316 mV
R6: Aquifer + GW + FeA_4	221 mV	144 mV	6 mV	32 mV	143 mV	73 mV
R7: aquifer + GW + $HgCl_2$ + FeA_4	303 mV	278 mV	-212 mV	-208 mV	-168 mV	-88 mV
R8: aquifer + GW + K-acetate + FeA_4	138 mV	-129 mV	-402 mV	-189 mV	-460 mV	-380 mV
R9: aquifer + GW + K-acetate + FeA_4 + Dd8301	106 mV	-398 mV	-246 mV	-229 mV	-241 mV	-198 mV

NOTES: 5 ml K-acetate (25%); Postgate C 10X concentrated; 10 g FeA4

T0: at time zero; T1: after 1 week; T4: after 1 month; T8: after 2 months; T12: after 3 months; T19: after 5 months.

Table 3: Ni Concentrations at Different Conditions from Groundwater from test site 2

Test conditions	T0		T1		T4		T8		T12	
	Tot.	Sol.	Tot.	Sol.	Tot.	Sol.	Tot.	Sol.	Tot.	Sol.
R1: aquifer+GW	62	54	52	45	80	81	56	53	65	74
R2: aquifer+GW+$HgCl_2$	54	45	44	42	68	70	93	63	69	74
R3: aquifer+GW+K-acetate	62	52	45	51	62	66	33	28	73	**16**
R4: aquifer+GW+ K-acetate+Dd8301	37	34	54	60	100	86	65	70	78	74
R5: aquifer+GW+ Postgate C+K-acetate+ Dd8301	424	82	270	103	**3.2**	**0.65**	**3.4**	**<2.5**	22	**1.1**
R6: aquifer+GW+FeA_4	57	51	51	34	**1.2**	**1.2**	**6.7**	**2.8**	**3.1**	**2.2**
R7: aquifer+GW+$HgCl_2$ +FeA_4	65	51	72	63	**6.5**	**1.0**	**16**	**2.8**	**7.5**	**1.2**
R8: aquifer+GW+K-acetate+FeA_4	48	33	28	**<20**	**1.3**	**1.9**	**4.6**	**<2.5**	**3.9**	**1.9**
R9: aquifer+GW+K-acetate+FeA_4+Dd8301	34	24	42	25	**1.3**	**7.7**	**9.2**	**<2.5**	28	**1.5**

NOTES:

Total: metals are measured in the groundwater after acidification; Sol.: metals are measured in the groundwater after filtration (metals bound to suspended solids are not measured).

5 ml K-acetate (25%); Postgate C 10X concentrated; 10 g FeA_4; Concentrations below the remediation standard (20 µg/L) are presented in bold.

T0: at time zero; T1 after 1 week; T4 after 1 month; T8 after 2 months; T12 after 3 months.

Both projects will continue by the start of column experiments under the most optimal conditions. These tests will allow to determine the kinetics of the remediation system and this information is necessary for the optimal design of the pilot project in the field. The results will be presented in a new publication.

At test site 3 the As concentrations were so high (< 6000 mg As/l) that no As removal could be obtained with the in situ bioprecipiation method. However in an other groundwater well where the As concentration in the groundwater was much lower a sulphate reducing potential could be indicated. These results are presented in figure 4. The results show that the addition of a electron donor as acetate will induce the sulphate reduction process. The reduction of a redox manipulating compound will also positively influence the arsenic immobilisation process.

Table 4. As concentrations at different conditions from groundwater from test site 3

Conditons	T0	T4	T6	T7	T16
groundwater	8480				
aquifer + groundwater	7170	*3780*	*971*	*4940*	2890
aquifer + groundwater + 0.5 mM $HgCl_2$	5910	*1560*	*1030*	*2060*	804
aquifer + groundwater + 1 ml K-acetate (25%)	5750	*3190*	*817*	*481*	605
aquifer + groundwater + 1 ml K-acetate (25%) + Dd8301	5560	*3420*	*679*	*145*	1120
aquifer + groundwater + Postgate C medium 10x + 1 ml K-acetate (25%) + Dd8301	5750	*1610*	*608*	*61*	246
aquifer + groundwater + Postgate C medium 10x + 1 ml K-acetate (25%)	5230	*1770*	*591*	*281*	151
aquifer + groundwater + RMC	5290	*2740*	*2250*	*1460*	398
aquifer + groundwater + 0.5 mM $HgCl_2$ + RMC	5730	*1550*	*1190*	*547*	156
aquifer + groundwater + RMC + 1 ml K-acetate (25%)	5070	*2710*	*805*	*140*	228
aquifer + groundwater + RMC + 1 ml K-acetate (25%) + Dd8301	6230	*2140*	*60*	*113*	136

NOTES:

RMC: redox manipulating compound; Tx : x number of weeks of incubation; xx : black precipitates of iron sulphide.

5. HEALTH AND SAFETY

For safety reasons no methanol was used and all the tests were performed with acetate as electron donor. The study must show now that the use of acetate is an applicable alternative. In the mean time many good results were also obtained with molasses and HRC® (Hydrogen Release Compounds). In a separate publication the results of a comparative study will be presented. This study will compare the obtained metal removal efficiencies, kinetics, irreversibility and costs related to the use of acetate, molasses and HRC®.

6. ENVIRONMENTAL IMPACTS

For environmental reasons, no molasses or compost extract was used. The product contained undetermined impurities that contaminated the ground after infiltration in the aquifer.

7. ENVIRONMENTAL IMPACTS

For environmental reasons some question marks were placed behind the use of molasse or compost extracts. These products contain undetermined impurities that will contaminate the groundwater with some unknown COD. Further studies are underway to evaluate the impact of compounds as molasses on the environment.

8. CONCLUSIONS

The batch tests showed for the three sites the feasibility of metals removal from groundwater by the induction in situ bioprecipitation. However some conditions are important. The sulphate concentration must be high enough (i.e. < 200 mg sulphate/l). otherwise only hydrogen can be used as electron donor. This can be achieved by the addition of HRC®. If the pH is low (< 4) than it becomes difficult to reduce the redox and to start the sulphate reducing process. In this case some redox manipulating compounds were added and once the redox dropped the sulphate reduction started. In case of high metals concentrations some toxicity can be inhibit the sulphate reduction process. However this is only the case with quite high metal or metalloid concentrations. In a going on pilot project the removal of metals followed the chemistry of the metal sulphides i.e. first precipitation of Cd, followed by Zn, Co and finally Ni.

It is very important to evaluate the irreversibility of the metal precipitation process. This can be done by a sequential extraction of the metals from the aquifer material. Studies are underway in order to evaluate the differences of the metal binding to the aquifer under aerobic versus anaerobic conditions.

9. REFERENCES

1. Corbisier, P. Thiry E., Masolijn A. and Diels L. (1994) Construction and development of metal ion biosensors. In Campbell A.K., Cricka L.J., Stanley P.E. eds. Bioluminescence and Chemoluminescence : Fundamentals and Applied Aspects. Chichester, New York, Brisbane, Toronto, Singapore. John Wiley and Sons pp150-155.

2. Corbisier, P., Thiry, E., Diels, L.(1996) Bacterial biosensors for the toxicity assessment of solid wastes, Environmental Toxicology and Water Quality: an international Journal, 11, 171-177.

3. Diels, L., Dong, Q., van der Lelie, D. Baeyens, W., Mergeay, M. (1995) The *czc* operon of *Alcaligenes eutrophus* CH34: from resistance mechanism to the removal of heavy metal. J. Ind. Microbiol. 14, 142-153.

4. Diels, L. (1997) Heavy metal bioremediation of soil in methods in Biotechnology, Vol. 2: Bioremediation Protocols, edited by O. Sheehan Humana Press Inc. Totowa, NJ.

5. Diels, L. (1990) Accumulation and precipitation of Cd and Zn ions by *Alcaligenes eutrophus* CH34 strains, in Biohydrometallurgy (Salley, J., McCready, R.G.L., and Wichlacs, P.Z., eds.), CANMET SP89-10, 369-377.

6. Mergeay, M. 1997. Microbial resources for bioremediation of sites polluted by heavy metals. In perspectives in Bioremediation p. 65-73 Ed. J.R. Wildcet al. Kluwer Academic Publishers, The Netherlands.

7. Van der Lelie, D., L. Diels, J. Vangronsveld, H. Clijsters. 1998. De metaalwoestijn herleeft. Het ingenieursblad 11/12.

Project No. 17 **GERBER Site**			
Location SERMAISE - Department of ESSONNE - ILE DE FRANCE Region	**Project Status** Final Report	**Media** Soil and groundwater	**Technology Type** Excavation and treatment of waste
Technical Contact Christian Militon ADEME BP 406 49004 ANGERS CEDEX 01 – France	**Project Dates** 06/1999 07/2002	**Contaminants** Complex contamination: solvents (BTEX and chlorinated); PCBs; phénols, phthalates; Pb, Zn	
	Project Size Full-scale		

The information in this project summary is current as of January 2002. Project 17 has ended, and risk assessment results are in hand.

1. INTRODUCTION

The GERBER site was operated since the beginning of the fifties until 1993 as a solvent regeneration plant. Until 1972, one or two lagoons have been used to dumps residues of the activities. In 1972-1973, an unknown but very significant quantity of drums was buried on the site. In 1983, the pollution of the drinking water well of the village of SERMAISE by chlorinated organics was attributed to the GERBER site located in the vicinity and a first preliminary investigation revealed buried drums with organic and chlorinated material.

Nothing happened during the following years because the polluter didn't have the financial capability to carry out significant depollution action. In 1992, in connection with the new legal and financial system created to deal with (orphan) site, a first clean up project was carried out by ADEME. The project consisted in the excavation of the main part of the buried drum area; 3,700 drums were excavated and treated and approximatively 14,000 tons of polluted soil was confined on the site. The treatment of this polluted soil was carried out in 1998-1999; 10,650 tons of polluted soil were treated on site by solvent washing and 5,850 tons that were less polluted were landfilled (hazardous waste landfill (classe 1)). The total cost of these first phases of cleanup is about 10 millions euros.

2. THE PREVIOUS PROJECT IN 1999

In addition to the first phase rehabilitation works presented above, it was clear that the remaining part of the site was still heavily polluted with not so much drums but with buried waste corresponding to the ancient lagoons and associated polluted soil and groundwater. Therefore an impact and risk assessment study was carried out in 1998 that characterized the remaining pollution:

- high concentrations of pollutants still cover 70% of the site
- highly contaminated soil was found to a depth of approximately 4-5 m
- total volume of polluted soil is estimated 50-75,000 m^3.

The impact study and modeling showed that the migration of the pollutants in the groundwater seems to be limited and that a two stages natural attenuation occurs: aerobic degradation of BTEX and then reductive dechlorination of chlorinated solvents. Based on these first results it was decided to prepare a new phase of evaluation and corrective action. The objectives of this new phase were to:

- improve the knowledge of the contamination source and to prepare the clean up of the remaining hot spots
- complete the evaluation of the transfer of the pollution in the air and in the groundwater with a detailed characterization of the mechanisms of the natural attenuation. Then, after this assessment of the efficiency and limits of the process of natural attenuation an additional project of in situ source reduction will be studied in order to have finally a restoration system able to reduce the risks to acceptable levels.

3. THE SITUATION IN 2002

The results from complementary investigations and the evolution of the quality of groundwaters shown:

- the discovery of around 2,000 drums full of hazardous wastes, buried just near the area excavated in 1992, but not detected during the previous investigations
- a previously undetected plume with VOH in the chalk water table which flows eastward out of the site, even though on the site and immediately downstream, the pollutants are the intermediate products resulting from the degradation of the VOH. The main pollutants found in the plume are the primary solvents, which characterize the site (TCE, PCE, and CCl_4). It is possible that the natural attenuation proved on the site is impossible in some areas out of the site

The new policy about remediation versus risk assessment conduct the French Ministry of Environment to stop the remediation to the end of 2002, waiting for the results of a new risk assessment study and a modeling, and asking for a better monitoring, because today the risks for human health and the environment are not considered as proved.

4. REFERENCE

Definition of corrective actions taking into account natural attenuation and risk assessment approach, former Etablissement Chimique du Hurepoix Site in SERMAISE -France - NATO CCMS meeting ANGERS May 1999.

Project No. 18 **SAFIRA**			
Location Bitterfeld, Germany	**Project Status** Final Report	**Contaminants** Chlorinated hydrocarbons, chlorobenzene	**Technology Type** Nine innovative approaches in situ for application
Technical Contact Dr. Holger Weiss UFZ-Centre for Environmental Research Permoserstrasse 15 D-04318 Leipzig Germany	**Project Dates** 7/1999 - 6/2002	**Media** Groundwater	
	Costs Documented? Yes	**Project Size** Pilot-scale	**Results Available?** Yes

Project 18 was completed in 2002.

1. INTRODUCTION

Approximately 75% of the drinking water in Germany is extracted from available groundwater resources. For this reason the protection of this essential resource is of a special interest. At many industrial sites in Germany inadequate waste disposal, leakages and war damages have led to the contamination of the subsurface with various contaminants, which in some instances led to groundwater contaminations on a regional scale.

The experiences of the last 20 years show, that standard hydraulic soil and groundwater remediation methods, such as pump-and-treat, in most cases do not lead to satisfactory results. This is even more true for large scale subsurface contaminations, where the source area of the contamination can either not exactly be localized or not be readily removed.

In order to avoid a permanent extraction and the subsequent treatment of contaminated groundwater, intensive research efforts in the last years have concentrated on the development of cheaper innovative in situ technologies, which focus on the removal or the degradation of contaminants in the aquifer. In contrast to ‘active’ technologies, which mainly focus on the source areas, ‘passive’ technologies are characterized by little or virtually no energy input during the remediation measure. Passive technologies have the advantage that operation costs, during the inevitably long remediation times, can be drastically reduced. The most advanced type of passive remediation techniques are in situ reactive barriers. For single contaminants or simple contaminant cocktails (e.g. PAH or VOC) reactive barriers are already implemented at several sites.

One example of a regional contamination of an aquifer is the Bitterfeld industrial complex in Saxony-Anhalt, Germany. For more than 100 years the activities in open cast lignite mining and the related chemical industries have had a serious impact on soil and groundwater quality. While the soil contamination is generally limited to the premises of the former industrial sites and landfills, the groundwater has regionally been contaminated over an area of approximately 25 km^2 with a total volume of approx. 200 million m^3.

2. BACKGROUND

The goal of SAFIRA (Sanierungs-Forschung in regional kontaminierten Aquiferen), a joint project of several research partners is to develop and to provide the necessary technologies and methodologies to demonstrate the successful implementation of in situ reactive barriers in regionally contaminated aquifers. The Bitterfeld–Wolfen region was chosen as an example of an area with a large scale and complex groundwater contamination.

Due to the extended time frame of field testing and the yet limited knowledge about the economical factors involved, the SAFIRA research project, in contrast to many other research projects, compares several potentially successful groundwater treatment technologies concomitantly. Research groups from the UFZ Leipzig, as well as the universities of Tübingen, Dresden, Kiel, Leipzig and Halle are involved in a joint research effort sponsored by the Federal Ministry of Science and Education (BMBF).

Within the framework of the remediation research program of the UFZ Leipzig there are also links to several international cooperation partners. Among them is a consortium from the Netherlands, led by TNO.

3. TECHNICAL CONCEPT

In order to address all important aspects of this innovative remediation approach the SAFIRA project is subdivided into several thematic branches (see Table 1). In addition to the aspects of scientific-technical implementation, economical evaluation as well as subsequent land use and legal aspects are being addressed. In the scope of the project, special emphasis is put on the possibility that innovative approaches and at least parts of the results obtained by the individual research partners can be transferred to other contaminant scenarios in and outside of Germany.

The overall aim of the research project includes:

- the development and the successive implementation of innovative low energy or passive water treatment technologies for mixed organic groundwater contaminations from prototypes to full-scale technical in situ application
- the technical-economical optimization of the individual technologies as well as possible combinations including the structural aspects of their implementation in in situ reactive barriers
- the demonstration of the longevity of the new technologies in the field and the determination of their actual operation cost
- the assessment of the legal and ecological aspects of the implementation of a reactive barrier system, exemplary for the Bitterfeld Region
- the development of economical application strategies for the most promising technologies

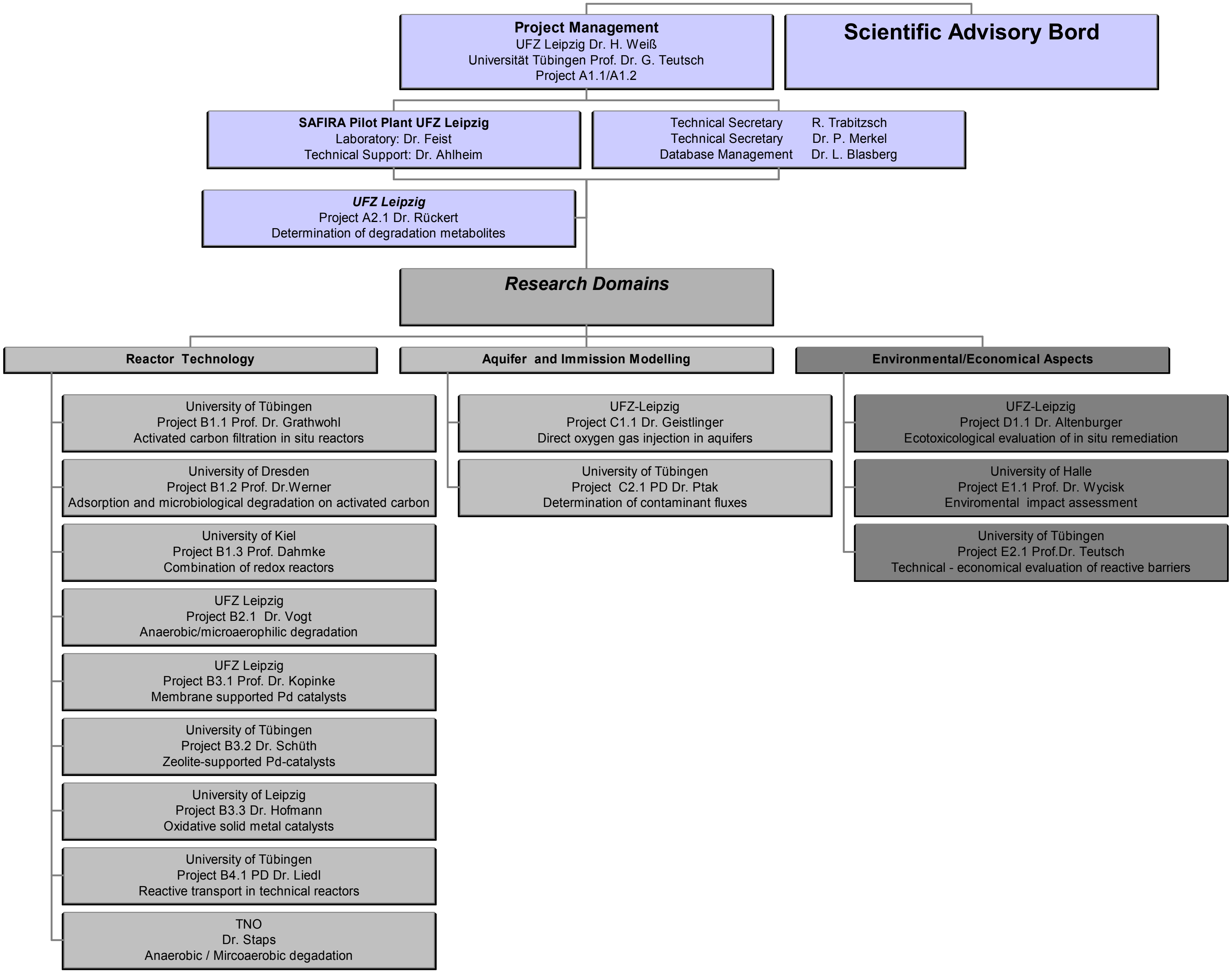
Based on either a successful performance in a mobile testing unit or on promising results in lab experiments the following eight approaches were selected to be tested in large scale in situ application:

1. Biodegradation of chlorinated hydrocarbons in a sequential anaerobic/micro-aerobic system
2. Adsorption and simultaneous microbiological degradation of chlorinated hydrocarbons on activated carbon
3. Degradation of chlorinated hydrocarbons using palladium coated Y-zeolites
4. Oxidizing metal catalysts
5. Membrane supported palladium catalysts
6. Redox-combination reactors
7. Activated carbon filtration
8. Anaerobic microbiological degradation of contaminants

One important aspect of the SAFIRA concept is the in situ pilot facility, which has to guarantee that the selected treatment technologies can be tested under realistic in situ conditions. The pilot facility in Bitterfeld, which houses a total of 20 reactors, consists of five shafts with a depth of 23 m, a diameter of 3 m and a shaft-to-shaft distance of 19 m, which were placed in a line perpendicular to the local groundwater flow direction and an on site laboratory building (Figsures 1 and 2). Construction at the site was completed in March 1999 and the pilot facility was officially opened in fall 1999.

Depending on the technologies of interest the sizes of the reactors range from 1-6 m in length and 150-1400 mm in diameter. The reactors are designed for a permanent system pressure of 3 bars and are operated in a flow-through mode from bottom to top. Flow rates can be varied, up to 400 l/h.

Table 1: SAFIRA Project is subdivided into several thematic research branches, each including related research projects.



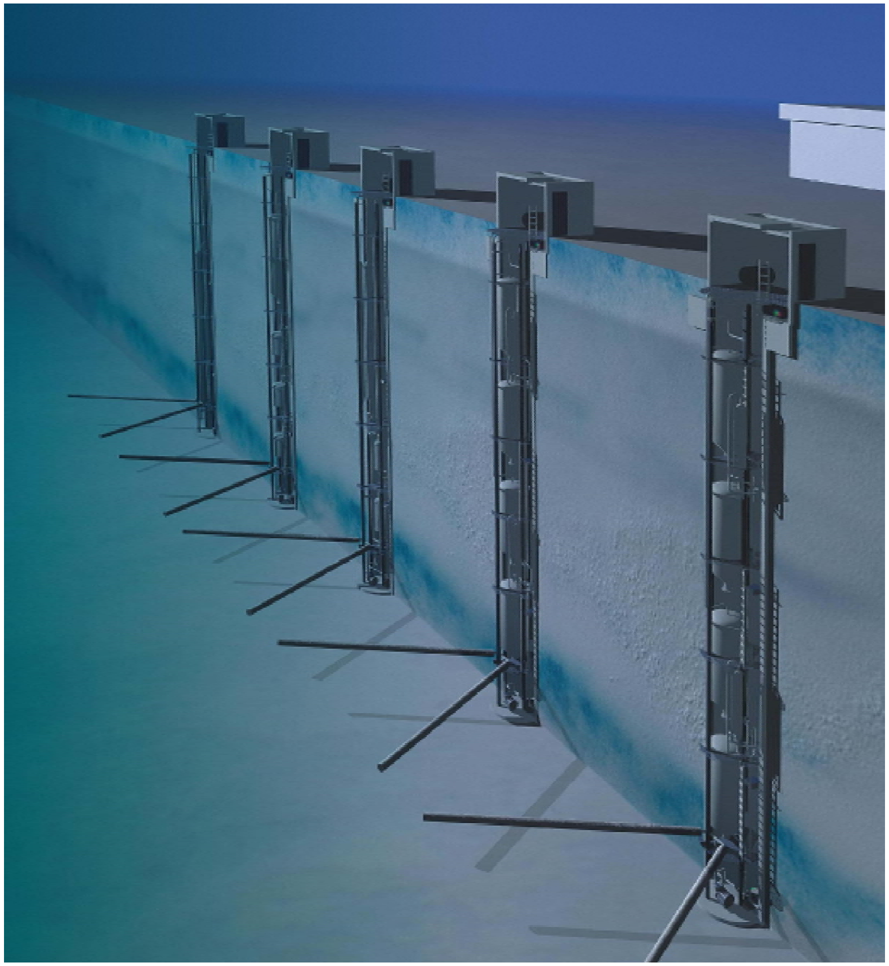


Figure 2: Schematic 3-D view of the well shafts and horizontal wells

Figure 1: The SAFIRA test site with the five well shaft housings on the left-hand side and the on-site laboratory building on the right-hand side

4. ANALYTICAL APPROACH

The groundwater for each shaft is collected by 2 horizontal wells of 10 m of length which were drilled at an angle of 60° (Figure 2).

The on site laboratory analyzes the major contaminants as well as the physical-chemical parameters (pH, conductivity, redox potential, temperature and oxygen content) AOX, TOC, and DOC directly at the site, thus minimizing possible alterations of the samples due to transport and storage.

Each experimental reactor has several regularly spaced sampling ports (depending on the size, the expected residence time of the groundwater and the process of interest) to monitor changes in groundwater composition along the passage through the reactor. Specific analyses are performed by the respective research teams. Due to the various technologies that are being applied at the site, special emphasis will be directed towards the determination of possible metabolites in the reactor outlets.

5. SOME RESULTS (UPDATED)

Over the last two years of large-scale in situ application the different research groups have been adjusting and optimizing their approaches in order to remediate the complex groundwater contamination at the site.

Activated Carbon:

Activated carbon filtration has performed well. No changes in the groundwater chemistry were observed as the reactor was percolated under in situ conditions. Occasional releases of particles were observed at early times and can cause particle bound phases contaminant release. The groundwater predominately contaminated with monochlorobenzene (MCB) was treated successfully over a time period of 2 years by the activated carbon filtration. In none of the in-situ operated activated carbon filters plugging, chemo- or biofouling was observed.

The loading of the activated carbon with the contaminants agreed very well with expectations from modeling (Breakthrough behavior of monochlorobenzene at ports in the GAC filters could be predicted using Freundlich Isotherms and coeffciants. The results of this long term investigation demonstrate, that in-situ activated carbon filtration can be sucessfully be used to remove hydrophobic, low solubility contaminants from groundwater.

Microbiology:

Under strictly anaerobic conditions, no definite degradation of MCB was observed. Adding hydrogen peroxide caused the degradation of MCB, accompanied by a clear increase of the number of cultivable aerobic MCB-degrading bacteria. The results point out that the oxygen released from hydrogen peroxide was almost completely consumed by bacteria for CB degradation.

Catalysis:

Zeolite as well as membrane-supported palladium catalysts showed a high capability of efficiently degrading aliphatic as well as aromatic chlorinated hydrocarbons (Schüth et al., 2000). However, Pd-catalysts are deactivated by the production of H_2S, due to the microbiological reduction of sulfate. Attempts to supress microbial activities to increase the longevity by applying periodical H_2O_2 pulses so far showed only limited success.

In order to prevent catalyst deactivation in the aqueous phase a new approach was developed using hollow fiber membrane contactors to transfer the contaminants into the gaseous phase. In contrast, for the gaseous phase efficient methods to remove sulfur containing compounds exist (e.g. zinc oxide, ZnO). Also the reaction rates are several orders of magnitude faster in the gaseous phase compared to the aqueous phase, due to the higher diffusion rates and higher catalyst temperature.

Using membrane contactors with large surface areas and applying a vacuum on the gas side, mass transfer limitations due to low Henry coefficients can potentially be overcome and much smaller systems are possible. In addition, using nitrogen as the strip gas, instead of ambient air, prevents oxygen from entering the system and thus minimises the risk of precipitations, as contaminated aquifer systems are in general anoxic.

Determination of Contaminant Fluxes:

A reliable contaminant mass flux estimation is especially important to design and scale reactors of in situ remediation schemes, where, as is also the case at the Bitterfeld site, a high spatial variability of contaminant concentrations in the subsurface leads to high uncertainties.

The method of integral estimation of contaminant fluxes downstream of a pollutant source zone employing the concentration time series measured in the discharge of pumping wells using the control plane approach, has been modified to include the 3-dimensional analysis of contaminant distribution in a contaminant plume. The new approach is now being applied to new data obtained at a series of pumping tests at the Bitterfeld site.

6. HEALTH AND SAFETY

Health and safety standards meet the high German working safety requirements. The shafts are permanently ventilated and air-conditioned. Each shafts is equipped redundant early warning systems for the case of fire, high carbon monoxide concentration, water flooding and reactor overpressure.

Entrance to the shafts is regulated by a pilot plant user manual and only allowed under inspection of the pilot plant staff and after an introduction into the safety features of the pilot plant.

7. ENVIRONMENTAL IMPACTS

In the design of the pilot plant minimal environmental impacts were already key aspects, as the innovative techniques were to be designed for an in situ application under natural aquifer conditions.

The horizontal wells at depths of about 20 m are designed to extract only highly contaminated aquifer water, without much disturbing the natural hydraulic regime.

Process water leaving the reactors is of course additionally treated in the on site waste water treatment facility, in order to prevent possible contaminantions in the process water leaving the pilot plant. All water leaving the site meets the required legal standards.

The contaminant concentrations at the inflow and the outflow of the reactors are checked regularly and a specially designed analytic program is being designed to check for metabolites in the effluent concentration.

The general ecotoxicological and environmental aspects of large in situ remediation approaches on the environment are covered by several research partners within the SAFIRA joint research project.

8. COSTS

The total costs for the implementation of the SAFIRA pilot plant was on the order of 11 Mio. DM. Maintenance and operation of the site, which is covered by the UFZ-Leipzig, amounts to approximately. 580.000 DM/a.

The German research partners involved in the SAFIRA project are sponsored by BMBF (Federal ministry of education and sciene).

9. CONCLUSIONS

- Several technologies (GAC/coupled redox systems) already showed their remediation potential under the anaerobic in situ conditions.Several technological approaches failed (e.g. anaerobic microbiological degradation, catalysis in the aqueous phase).

  Catalytic degradation of chlorinated hydrocarbons can be an efficient way to remediate MCB and other chlorinated hydrocarbons under more favorable hydrochemical groundwater conditions.

  Microbiological degradation of MCB under anoxic conditions could not be confirmed at the test site. However new approaches have already been tested in the lab and in mobile treatment units under in situ conditions. No single (successful) technology will be able to deal with complex contaminant cocktails.

- Combinations of several approaches are needed in order to address the problems at complex sites (2nd generation of integrated technologies). Due to a high spatial variability of contaminant concentrations as well as of composition at the Bitterfeld site, expected contaminant fluxes towards a remediation site need to be characterized in detail prior to the design of remedial action.Tools for the technical and economical evaluation are presently developed and will be ready for application at the end of phase 1. Outlook

- Starting 2003, the Infrastructure, Personal- and Operation Costs of the SAFIRA Sites is introduced into HGF-Leistungskategorie II ‚National and international Science Infrastructure‘.

- This Classification makes it possible to support the a.m. sites as a research platform of the international Scientific Community.The platform is to be used by more than 50% external users (non UFZ Researchers) and is supervised by an external scientific board.The facilities are available for interested researchers at at a small maintenance fee.

10. REFERENCES

1. BOCKELMANN, A., PTAK, T. TEUTSCH,G. (2001): An analytical quantification of and natural attenuation rate constants at a former gasworks site, Journal of Contaminant Hydrology, (53),429-453.

2. KÖBER. R, EBERT, M. SCHÄFER, D., DAHMKE, A. (2001a): Kombination vonFe^0 und Aktivkohle in Reaktionswänden zur Sanierung komplexer Mischkontaminantionen im Grundwasser, altlasten spektrum, 2/2001, 91-95.

3. KÖBER. R., EBERT, M. SCHÄFER, D., DAHMKE, A. (2001B): Kombination von Fe^0 Reaktionswänden und ORC zur Behandlung komplexer Mischkontaminationen im Grundwasser, Terra Tech, 3/2001, 1-6.

4. MERKEL, P., WEIß, H., TEUTSCH, G., RIJNAARTS, H. (2000): Innovative Reactive Barrier Technologies for Regional Contaminated Groundwater, In: Proceed. of the 7th International FZK/TNO Concerence on Contaminated Soil, 18-22 September 2000, Leipzig, Thomas Telford, S.532-540.

5. SCHÜTH, C., DISSER, S., SCHÜTH, F., REINHARD, M. (2000): Tailoring Catalysts for Hydrodechlorinating Chlorinated Hydrocarbon Contaminants in Groundwater, Applied Catalysis B: Environmental, 28, 147-152.

6. WEIß, H. RIJNAARTS, H., STAPS, S., MERKEL P. (2000)(EDS.): SAFIRA Abstracts of the workshop of November 17-18, 1999 at Bitterfeld /Germany, UFZ Bericht Nr. 23/2000.

7. Webpage http://safira.ufz.de/

Scientific/technological approaches	**Research contacts**
Project and test site management	weiss@pro.ufz.de georg.teutsch@uni-tuebingen.de
Determination of metabolites and degradation products of in situ technologies	weiss@pro.ufz.de
The Influence of Groundwater Specific Parameters on the Performance of In Situ Reactors based on the Example of In-Situ Activated-Carbon-Filtration	peter.grathwohl@uni-tuebingen.de
Elimination of volatile organic compounds by adsorption and simultaneous microbiological degradation on activated carbon	pwerner@arcs.urz.tu-dresden.de
Development of coupled in situ-reactors and optimisation of the geochemical processes downstream of different in situ-reactor systems	ad@gpi.uni-kiel.de
Microbiological in situ remediation of aquifers contaminated with chloroorganic contaminants at the model site Bitterfeld using autochthonous bacteria	vogt@umb.ufz.de
Dechlorination of chlorohydrocarbons in groundwater by electrochemical and catalytic reactions	kopinke@san.ufz.de
Zeolite-supported catalysts for hydrodehalogenation of contaminants in groundwater	schueth@uni-tuebingen.de
Degradation of halogenated organic pollutants by catalytic oxidation	hofmann@inc.uni-leipzig.de
Reactive transport in technical reactors	rudolf.liedl@uni-tuebingen.de
Direct oxygen injection into natural aquifer sections and artificial porous media: Gas-water-dynamics and heterogeneous reactions between mixed fluid phases	geist@hdg.ufz.de
Determination of the contaminant loads in contaminated aquifers for the design of in situ reactors	thomas.ptak@uni-tuebingen.de
Ecotoxicological determination of the performance of in situ treatment measures in contaminated aquifers	ra@uoe.ufz.de
Development of model approaches to assess the general effects of groundwater remediations by permeable reactive barriers	wycisk@geologie.uni-halle.de
Technical and environmental-econonmical assessment of reactive barriers	georg.teutsch@uni-tuebingen.de
Biodegradation of chloroethenes and chlorobenzenes in a two-phase anaerobic/microaerobic treatment zone system	s.staps@mep.tno.nl

Project No. 19

Succesive Extraction-Decontamination of Leather Tanning Waste Deposited Soil

Location	**Project Dates**	**Report Status**	**Contaminants**
University of Istanbul	Accepted 1998 Final Report 2001	Interim	Organic and inorganic
Technical Contact	**Costs Documented?**	**Results Available**	**Project Size**
Dr. Erol Erçag University of Istanbul Faculty of Engineering, Department of Chemistry Avcilar, 34850 Istanbul, Turkey Tel: 0212 593 84 7, Ext. 1191 Fax: 0212 591 19 98 E-mail:Ercag@istanbul.edu.tr	No	None	Laboratory/field

Information in this project is current as of January 2002.

1. INTRODUCTION

Since old leather tanning industries have been moved from a central region to the outskirts of Istanbul, namely from Zeytinburnu to Tuzla of Istanbul, considerable land into which the tanning wastes were dumped over years are now waiting to be reused. Now the Greater City Municipality of Istanbul is considering this emptied region for recreational and housing purposes. This region now poses considerable health hazard for the potential future users of this land.

2. AIM

This project was purported to perform the treatability study of the contaminated soil at Zeytinburnu.

3. METHOD

Sampling of soil over the abandoned tanning industrial area will be made, and the organic and inorganic contaminants in the soil will be analysed. Volatile organic compounds (VOCs) will be analysed by a photoionization dectector capable of detecting more than 250 chemicals.

According to the types of organic (e.g., additives and modification agents) and inorganic (e.g., chromium, sulfide, etc.) constituents present as contaminants, a treatability study of soil consisting of organic extraction with suitable solvent (e.g., methylene chloride) followed by acid leaching of toxic heavy metals will be carried out. Both synthetic and real soil samples will be carried out to optimize solvent, acid, leachant concentration, solids-to liquid ratio and so on.

Currently, points from which soil samples are to be taken have already been determined. Several samples are to be taken from the same point according to the distance to the surface. The depth from which samples are planned to be taken will be roughly 1 meter at maximum. At the same sampling positions, VOC measurements will also be made.

4. RESULTS

Not available.

5. COSTS, HEALTH, AND SAFETY

Not yet available.

6. CONCLUSIONS

There are insufficient data available to draw any meaningful conclusions.

7. REFERENCES

Not applicable.

Project No. 20

Innovative Treatment Technologies: A Summary of Work Completed on a DNAPL Site at Cape Canaveral, Florida

Location	**Project Status**	**Media**	**Technology Type**
Cape Canaveral, Florida	Completed	Groundwater	In situ chemical oxidation In situ thermal remediation with six phase heating In situ thermal remediation and steam injection
Technical Contact	**Project Dates**	**Contaminants**	
Thomas O. Early Oak Ridge National Laboratory P.O. Box 2008, MS 6038 Oak Ridge, TN 37831-6038 Tel: (865) 576-2103 (Office) Fax: (865) 574-7420		Chlorinated solvent DNAPLs	
	Costs Documented?	**Project Size**	**Results Available?**
	October 2002	Field Treatability Testing	Spring 2002

Project 20 was completed in 2002.

1. INTRODUCTION

Dense non-aqueous phase liquids (DNAPLs) pose a serious, long-term threat to groundwater contamination due to their toxicity, limited solubility in ground water, and significant migration potential in soil gas, groundwater, and/or as separate phase liquids. DNAPL chemicals, particularly chlorinated solvents, are among the most common of environmental contamination problems in the United States as well as for most industrialized countries. There are thousands of DNAPL-contaminated sites in the United States, often at contaminant volumes that are difficult to detect, but in quantities that can represent significant sources of groundwater contamination. Many federal, state, and local governmental agencies as well as private-sector sites are impacted by this environmental problem. The U.S. Office of Management and Budget estimates that the federal government alone will spend billions of dollars for environmental clean up of DNAPL contamination.

There are many uncertainties associated with treatment of DNAPL sources in the subsurface. First, it is difficult to define accurately the location and distribution of the DNAPL. Secondly, the aggressive, innovative treatment technologies currently being marketed have not been subjected to rigorous evaluation in order to determine their performance and cost of application under a variety of site conditions. It is difficult to make meaningful comparisons of either performance or cost among these technologies because of the variable conditions present at the demonstration sites and inconsistent objectives of the individual demonstrations.

2. TECHNICAL CONCEPT

In 1998, a multiagency consortium (Interagency DNAPL Consortium, or IDC) was organized to address cost and performance issues related to DNAPL source treatment using innovative technologies. The U.S. Department of Energy/Office of Environmental Management (DOE/EM), the U.S. Department of Defense (DOD) through the Air Force Research Laboratory in cooperation with the 45th Space Wing, the National Aeronautics and Space Administration (NASA) and the U.S. Environmental Protection Agency (EPA) agreed to cooperate in demonstrating innovative DNAPL remediation and characterization technologies at a NASA site on Cape Canaveral Air Station (Launch Complex 34), Cape Canaveral, FL. The Naval Facilities Engineering Service Center of the U.S. Navy joined the IDC several years later.

The IDC was formed to:

- Address a serous, wide-spread and shared environmental problem adversely affecting many U.S. federal agencies (e.g., DOE, EPA, DOD, NASA, Department of Interior, Department of Agriculture);
- Accelerate both the demonstration and deployment of DNAPL remediation, characterization and monitoring technologies for the purpose of reducing the perceived technology risk associated with these technologies;
- Increase regulatory and user acceptance of these technologies by providing documented, cost and performance data; and
- Provide increased opportunities to test new sensors designed to support in situ remediation of DNAPL contamination problems.

In order to conduct the side-by-side demonstrations, a Management Team was organized consisting of representatives from DOE, NASA, USAF, DOD, and EPA. The Team is a collaborative decision-making body that draws upon the strengths of each agency to solve problems associated with the project. The Team formed a Technical Advisory Group (TAG) whose members came from industry, academia and federal agencies and are experts on DNAPLs and DNAPL treatment technologies. The TAG made recommendations as to the treatment technologies to use and participated in review of work plans and technical reports for each of the demonstrations. With the assistance of the TAG, the Management Team selected three of the most promising remediation technologies for deployment and evaluation at Launch Complex 34: in situ chemical oxidation with potassium permanganate, electrical resistance heating, and thermal treatment using steam.

3. SITE CONDITIONS

NASA's Launch Complex 34 was selected as the test site following an intensive evaluation by a variety of DNAPL characterization methods. A zone of DNAPL contamination was discovered in a region covering about 0.12 ha in front of a building in which TCE was used to clean rocket engine parts. It is believed that TCE reached the subsurface through leaking floor drains and piping as well as by direct discharge to the ground surface. DNAPL was found to extend to a depth of ~13.7 m below ground surface where a clay aquitard is encountered. Extensive contamination by DNAPL also was discovered underlying the building, but the extent of this contamination was not determined. The site in front of the building was subdivided into three treatment cells, each ~15 X 23 m in size (Figure 1). A small part of each cell extended under the building.

The lithologies present at the test site are illustrated in a cross section in Figure 2 and include the following units in ascending order: the Lower Confining Unit (LCU) that occurs at a depth of about 13.7 m and is believed to be a barrier to downward DNAPL migration, the Lower Sand Unit (LSU), the Middle Fine-Grain Unit (MFGU), and the Upper Sand Unit (USU). The MFGU is about a factor of 10 less permeable than either the USU or LSU. The water table surface occurs at a depth of about 2 m, but is somewhat variable depending on the amount of rainfall.

The total masses of TCE (dissolved, sorbed, and separate phase) and TCE as DNAPL in each cell were determined by collecting and analyzing continuous soil cores. An unaligned systematic sampling design was used to select the core locations. The footprint of each cell was subdivided into 12 equal grid elements. Each grid element was further subdivided into 16 equal sub-areas. One sub-area in each of the grid elements was selected randomly as locations of soil cores. Therefore, 12 cores were collected in each cell. Each 0.5 m section of core was analyzed for its total TCE content. Consequently, nearly 300 samples were collected from each cell and used to construct a 3-D model of the distribution of TCE. From these data the mass of total TCE and TCE as DNAPL within each cell was computed and the results are presented in Table 1. The soil analytical data can be evaluated by several different methods and the results for each are provided in the table. First, the TCE concentrations were contoured using the EarthVision software and the mass of TCE and DNAPL was computed from the volume and concentration of the isoconcentration shells within the cells. Alternatively, we used a kriging method that takes into account the spatial variability and uncertainty of the TCE distribution to estimate its total mass within the cells.

Kriging yields a mass estimate and uncertainty in that mass for the desired confidence interval (80%). We did not apply kriging to determine the mass of DNAPL.

4. ANALYTICAL APPROACH

4.1 In Situ Chemical Oxidation (ISCO)

In situ oxidation using potassium permanganate is a potentially fast and low cost solution for the destruction of chlorinated ethylenes, BTEX (benzene, toluene, ethylbenzene, and xylene) and simple polycyclic aromatic hydrocarbons. In particular, potassium permanganate reacts effectively with the double bonds in chlorinated ethylenes such as trichloroethylene (TCE), perchloroethylene, dichloroethylene isomers, and vinyl chloride. It is effective for the remediation of DNAPL, absorbed and dissolved phase contaminants and produces innocuous breakdown products such as CO_2, chloride ions and $MnO_2(s)$. The permanganate solution typically is applied by injection at a concentration of one to three percent. This solution is easily handled, mixed and injected and is non-toxic and non-hazardous.

Bench-scale laboratory tests of potassium permanganate with TCE have resulted in up to a 90% reduction of the contaminant in four hours of treatment. The effectiveness of the in situ injection of permanganate is a function of the reaction kinetics, the transport and contact between potassium permanganate and the contaminant, as well as competitive reactions with other oxidizable species (e.g., iron, natural organics). The effective use of this remedial technology requires an engineered approach for maximizing the contact between potassium permanganate and the target contaminant. As with many technologies, low permeability and heterogeneity of soils present a challenge and require a carefully designed application system.

At Cape Canaveral, the ISCO demonstration took place during between August, 1999 and May, 2000. Permanganate injection occurred in three phases. In each phase, potassium permanganate solution was pumped to a manifold and thereafter injected into the subsurface through a number of soil lances that were advanced in 0.6 m increments by direct push methods. Injection occurred to a total depth of about 13.7 m. The location of the injection points was determined in such a way that the zones of influence for neighboring injections overlapped with the intent of causing complete invasion of the DNAPL contaminated zone.

4.2 In Situ Thermal Remediation with Six Phase Heating (SPH)

The Six Phase Heating (SPH) technology removes contaminants from soil and groundwater by resistively heating the soil matrix, groundwater, and contaminants in the treated region. In SPH normal three-phase electricity is split into six separate phases, which is delivered to the subsurface through metal electrodes arranged in a hexagonal array. As the temperature of the subsurface increases, a point is reached when boiling of the TCE-groundwater system occurs (~73 deg. C at atmospheric pressure). In principle, a combination of direct volatilization and steam stripping drives contaminants to the vadose zone where it is captured by vapor recovery wells for removal and treatment in an ex situ treatment system.

The SPH demonstration at Cape Canaveral began in August, 1999 and continued with several interruptions until July, 2000. The system was shut down during October and November, 1999 due to the impact of several hurricanes and tropical storms that caused equipment damage and unanticipated releases of TCE to surface water. Another shutdown occurred during the spring of 2000 due to replacement of an electrical generator.

Recent laboratory and field investigations of thermal treatment technologies indicate that breakdown of TCE and other chlorinated solvents can occur. Hydrous pyrolysis oxidation (HPO) is an example of such a process in which the oxidative breakdown of TCE occurs rapidly at steam temperatures yielding non-toxic byproducts such as CO_2 and chloride ions. Therefore, with the application of SPH it is anticipated that some TCE will be extracted as vapor and treated at the surface while another component will be totally mineralized in situ.

4.3 In Situ Thermal Remediation with Steam Injection

Thermal remediation by steam injection is another thermal treatment method used at Cape Canaveral. We used a suite of technologies developed by the University of California and Lawrence Livermore National Laboratory that includes Steam Enhanced Extraction (SEE) and Dynamic Underground Stripping and Hydrous Pyrolysis/Oxidation (DUS/HPO). The steam treatment system at Launch Complex 34 used boilers to generate steam, which was then pumped into the subsurface through centrally located injection wells. The steam front progressed outward from the injection wells to the periphery of the cell volatilizing and mobilizing contaminants as it moved. A network of extraction wells was located along the perimeter of the cell and contaminants were vacuumed to the surface for treatment. The initial application of steam to the subsurface at Launch Complex 34 was accompanied by co-injection of air. Air is a non-condensable gas and studies conducted by Dr. Kent Udell (U.C. Berkeley) show that injecting it with the steam helps prevent formation at the steam-groundwater interface of a condensation front of TCE DNAPL that might be mobilized downward.

At Launch Complex 34, a network of thermocouples was used to produce a 3-D image of temperature throughout the treatment cell as well as in a zone surrounding the cell. Careful monitoring of temperatures helped to evaluate the progression of the steam front and also helped confirm that the steam-TCE vapor mixture did not migrate beyond the extraction wells at the edge of the cell.

As discussed above, HPO is a companion process to thermal treatment technologies such as SPH and DUS. We anticipated some in situ degradation of TCE due to HPO during the steam treatment demonstration.

The steam demonstration began in July 2001 and continued until mid-December, 2001.

5. RESULTS

5.1 ISCO

Table 1 gives the results of the pre- and post-demonstration sampling of the oxidation test cell and an estimate of TCE removal from the cell. The contouring results indicate that the oxidation cell originally contained in excess of 6000 kg of TCE (>5000 kg of DNAPL). Following the ISCO demonstration the residual mass of TCE was 1100 kg (~800 kg DNAPL). This suggests an apparent TCE removal efficiency of 82% for TCE (84% for DNAPL). Kriging of the same soil core data yields somewhat different results. At the 80% confidence interval (CI) the ranges of values for the TCE mass both before and after the demonstration are higher than for the contouring method. In general, the kriging method should provide a better estimate of contaminant mass because it uses spatial correlations among the TCE data and makes inferences about TCE concentrations at unsampled points.

The spatial distribution of TCE in the oxidation cell following the ISCO demonstration indicates that a sharp decline in the soil TCE content occurred for each of the lithologic units and that the only region where treatment was not effective was on the southwestern corner of the cell, which underlies the building.

Table 2 gives the mass of $KMnO_4$ and volume of solution injected for each phase of treatment. The cumulative volume of fluid injected represents over three pore volumes of the test cell. Consequently, it is apparent that there was significant displacement of contaminated groundwater within the cell to regions beyond the cell boundary. During the period of peak permanganate injection (April 2000), a steep hydraulic gradient centered on the cell was developed, especially in the LSU. We believe that the duration of the elevated heads was short-lived owing to the high transmissivity of the lithologic units. We attempted to evaluate the impact of groundwater displacement to see if DNAPL might have been mobilized outside of the cell. However, the region around the cell has significant TCE contamination, so it is difficult to determine if significant changes in the amount and distribution of DNAPL in this zone occurred due to the ISCO demonstration.

5.2 SPH

Table 1 presents the “before” and “after” mass estimates for Total TCE and TCE DNAPL in the SPH test cell. The contoured data indicate that the mass of TCE prior to the SPH demonstration was ~11,300 kg (~10,500 kg DNAPL). The post-demonstration mass of TCE was ~1100 kg (~340 kg DNAPL). These data suggest an apparent removal efficiency of TCE of 90% (97% for DNAPL). As for the oxidation cell, kriging of the soil data are provided for comparison and are believed to yield more defensible TCE mass estimates. As for the ISCO demonstration, the region of the cell with most residual contamination after the SPH demonstration appears to underlie the Engineering Support Building.

The vapor recovery system affords an opportunity to measure the amount of TCE recovered from the cell. During the period of operation, ~1950 kg of TCE was recovered along with a small amount of TCE degradation products. The recovered TCE accounts for approximately 17% of the TCE thought to have been in the test cell. The amount of TCE left in the cell following the demonstration along with what was recovered by the vapor extraction system accounts for only ~27% of the total. We believe that there are several possible explanations for the “missing” mass of TCE:

- The mass estimates for TCE in the cell are grossly in error
- Some TCE extracted into the vapor treatment system escaped before being measured
- Some TCE vapor escaped into the atmosphere by fugitive emissions through the surface of the test cell during the demonstration
- Some TCE migrated laterally in the subsurface beyond the boundaries of the test cell
- Some TCE was destroyed in situ by HPO or other types of reactions

The results of this demonstration are still being evaluated, but we believe that several of these possible explanations are the most likely cause for the missing mass. Specifically, we believe that some unknown quantity of TCE migrated beyond the cell boundary in the subsurface. Some of the thermocouple data indicate that due to its lower permeability the MFGU may not permit an easy pathway for vertical migration of steam and TCE vapor to the USU. Consequently, we believe that lateral migration of some vapor and contaminated groundwater probably occurred to regions outside of the cell boundary near the LSU-MFGU contact. There is evidence that shallow groundwater flow also occurred through the SPH cell due to the heavy rains associated with tropical storms during September-October 1999. In addition, displacement of contaminated groundwater in the ISCO cell due to $KMnO_4$ injection may have contributed to some lateral flow in the SPH cell. Together, these mechanisms are believed to have resulted in lateral migration of contamination outside of the cell.

We observed a great increase in dissolved chloride content in groundwater within the cell following the demonstration suggesting that oxidation or other types of degradation reactions mineralized a significant amount of TCE releasing chloride to groundwater. However, boiling of groundwater may account for some of the observed increase. Assuming that increases in dissolved chloride concentrations are from TCE mineralization then it should be possible to estimate the amount of TCE that degraded. Unfortunately, lateral migration of chloride-enriched groundwater from the SPH cell during the demonstration impacted a relatively large region to the northwest of the cell making such mass estimates highly uncertain.

Our information on fugitive emissions is confined to a series of short-term measurements using vapor-trapping chambers placed on the ground surface. The results are not definitive, but we cannot rule out this process as contributing to the missing TCE mass.

5.3 Steam Treatment

The treatment cell for the steam demonstration contained an estimated 10,400 kg of TCE (~9,300 kg of DNAPL) prior to the beginning of steam injection. At the conclusion of the demonstration soil core analyses indicate that between 80 and 90% of the TCE had been removed from the cell by a combination of vapor extraction and in situ oxidative breakdown (i.e. HPO). Nearly 90% of the DNAPL was gone from the cell. Table 1 summarizes the data for the two mass estimation methods used. The regions of the cell where TCE removal was least effective was underlying the Engineering Support Building (USU and MFGU) and along the western and northwestern boundaries of the cell (LSU).

Maintaining hydraulic control at the cell boundary was one of the objectives of this demonstration to avoid the possibility of TCE migration beyond the cell. The vendor accomplished this goal by injecting steam in the central part of cell and extracting vapor (steam-air-TCE) and groundwater from recovery wells located along the cell perimeter. We verified that hydraulic control was maintained by monitoring a network of thermocouples located along the cell perimeter at discrete depths from the surface to the top of the LCU (~ 13.7m deep). We installed an additional thermocouple network around the cell ~8m beyond the perimeter. Collectively, the thermal data verified that nearly the entire cell was heated sufficiently to vaporize TCE, but there was little thermal impact beyond the cell boundary.

During the demonstration, over 15,000 m^3 of groundwater was pumped from the recovery wells representing a volume equal to about 11 times the pore volume of the cell. This large volume of water is a consequence of using recovery wells along the cell perimeter where a large amount of groundwater from outside of the cell was pumped. Because the steam cell is surrounded by contaminated soil and groundwater, the pumping wells probably imported a significant amount of TCE in addition to that recovered from within the cell itself (due to thermal treatment) that had to be handled by the above-ground treatment system.

Although we monitored TCE in the waste stream of the recovery wells, a breakdown of equipment during the early part of the demonstration when contaminant recovery was likely to be high resulted in uncertainty for the overall mass balance. We were also unable to confirm significant increase in the dissolved chloride in groundwater due to HPO because the ambient pre-demonstration chloride levels were already high. Finally, as for the SPH demonstration, we looked for fugitive emissions of TCE with measurements with vapor-trapping chambers at a number of locations within and surrounding the cell perimeter. Some of these measurements indicated elevated TCE vapor emission, but due to the short duration of the measurements it is not possible to estimate losses by vapor transport. Collectively, these observations limit our ability to establish a mass balance, but the results in Table 1 coupled with thermal monitoring data indicate significant mass removal/destruction with no apparent uncontrolled TCE migration from the cell.

6. HEALTH AND SAFETY

All of the technologies tested at Launch Complex 34 have been deployed at other sites over a period of at least several years. Consequently, while certain precautions must be taken, most health and safety issues were anticipated and addressed successfully.

For ISCO, $KMnO_4$ is a stable oxidant and does not present unusual handling problems. However, precautions must be taken to avoid skin contact with the $KMnO_4$ by wearing Tyvek suits and by maintaining a solution of vinegar, hydrogen peroxide, and water to neutralize oxidant spills on the ground or clothing.

The SPH technology has several potential areas where health and safety considerations must be addressed. Foremost among these is controlling the transport and distribution of high voltages (up to 500 V) used to power the electrodes. The vendor was successful in insulating the ground surface from the current passing through the aquifer. Secondly, when the water in the aquifer is at the boiling point, monitoring wells screened in the heated zone either must remain sealed or must be vented to the off gas treatment system. Opening a well cap under these conditions leads to pressure release and flash boiling of groundwater and presents a threat of serious burns to personnel.

For the steam technology the major health and safety issue is related to the handling of steam and the potential for burns.

7. ENVIRONMENTAL IMPACTS

There are two major sources of environmental impact from the application of these technologies. First, with ISCO an industrial grade of $KMnO_4$ was used to make the oxidant solution with a concentration up to ~3% by weight. This grade of permanganate contains trace amounts of a number of constituents. At a concentration of 1-2%, the solution exceeds the drinking water standard for several elements (e.g. Cr) and approval was required from the State of Florida to permit injection. In addition, it is possible that the permanganate solution can oxidize and mobilize indigenous metals associated with the geologic media. These effects are believed to be short-lived.

The second type of environmental effect is related to the impact of the oxidant or thermal treatment process on the microbiological community present in the subsurface. In order to evaluate this impact, we sampled the soil in each cell prior and subsequent to treatment and evaluated changes in the microbial population. We are in the process of collecting and evaluating these data, but it seems clear that application of the technologies caused a net reduction in the overall numbers of microbes. However, we do not know at this time how different types of bacteria were affected by the demonstration.

8. COSTS

Table 3 presents a summary of the cost of applying the three technologies at Cape Canaveral. The cost is very sensitive to several factors. For all of the technologies demonstrated at Cape Canaveral, field operations account for the largest cost element. In addition, for ISCO, the cost is strongly related to the amount of TCE that needs to be oxidized and to the oxidant demand from the media itself. The oxidation test cell at Cape Canaveral contained ~6000kg of TCE, requiring a rather large amount of $KMnO_4$ which contributed significantly to the cost.

The operational cost factors for both the SPH and steam technologies include the fuel or electricity that drives the thermal process. However, in contrast to ISCO, the incremental cost of vaporizing the TCE is inconsequential. Therefore, the amount of TCE in the cell is not a significant cost driver.

The costs incurred to apply these technologies depend on the specific way it is deployed (e.g. delivery system used, performance target to be achieved, etc.). What is shown in Table 3 is specific to the design of the demonstrations that were conducted. These costs do not reflect two important factors: (a) if treatment were for the entire source area instead of just a cell within a larger zone of contamination, then there would likely be an economy of scale and the design for deployment of the technology might be significantly different, and (b) lessons learned from these and other demonstrations will likely promote optimization of design with resultant cost savings.

9. LESSONS LEARNED

As a result of conducting these three technology demonstrations and the associated characterization work that supported them we have identified several major lessons that should be understood:

- Inadequate recognition of important design and implementation features of the technologies can result in problems. For example, the ISCO demonstration involved injection of ~three cell pore volumes of permanganate solution that resulted in significant, short-term hydraulic mounding within the cell, fluid migration beyond the ISCO cell boundary, and impacts on neighboring demonstrations. A fluid recirculation system would have avoided this problem.

- Constraints placed on the demonstrations by the IDC to facilitate their side-by-side deployment led to a non-optimal design for the steam injection demonstration. The steam demonstration was deployed with central injection of steam/air and fluid recovery at the cell perimeter (to maintain hydraulic control), whereas the opposite approach would be used for complete source treatment under normal circumstances resulting in extraction of much less groundwater requiring treatment..
- The potential impact of site geology on the performance of the technology must be considered. For example, monitoring associated with the SPH demonstration illustrated that the MFGU acted as a partial barrier to vertical migration of vapor (steam + TCE) and heated water from below. As a result, lateral migration of contamination beyond the SPH cell boundary probably occurred at the base of the MFGU.
- Even at this simple site, the difficulty of achieving a mass balance of TCE (and the uncertainties associated with making such estimates) suggests that less emphasis should be placed on this objective. Even with extensive coring and analyses, uncertainties on the order of 10-30% at the 80% CI were common. Therefore, it seems reasonable to consider reducing the amount of characterization aimed at achieving an accurate estimate of contaminant mass and focus more attention on measuring the impact of source treatment (e.g. future mass fluxes).
- Cost comparisons reflect the manner in which the technologies were designed and deployed (reflecting constraints placed on vendors by their contracts) and as such may be somewhat artificial. For example, the enormous amount of water recovered during the steam demonstration (requiring treatment and disposal) was a direct result of the design used to maintain hydraulic control at the cell boundary.

10. CONCLUSIONS

Demonstrations of the three DNAPL source remediation technologies used at Cape Canaveral are providing a rich source of data that will continue to be evaluated in the future. We have completed collecting most of the monitoring data associated with the demonstrations, although additional microbiological data still are being collected and evaluated.

In general, we can conclude that all of the demonstrations were successful in removing and/or destroying a significant fraction of the TCE from their respective test cells. Treatment efficiencies equal to or exceeding 80% for SPH, from 62-84% for ISCO, and 80-90% for steam are indicated by the data. There is an indication that for the SPH demonstration perhaps as much as ~70% of the TCE cannot be accounted for. There is evidence that some of the “missing” mass was destroyed by in situ oxidative reactions, although some may have migrated laterally outside of the cell. In addition, fugitive emission of TCE vapor through the ground surface cannot be ruled out.

These demonstrations and the associated cost and performance data are only one step of a planned effort to test innovative DNAPL source remediation technologies under a variety of site conditions. Based on the Cape Canaveral and other related demonstrations, we recognize that a number of scientific and engineering questions about the technologies remain to be resolved. Further testing and scientific inquiry are the only way in which these questions can be answered.

Table 1: Estimated masses of total TCE, DNAPL, and cleanup efficiency from application of the ISCO, SPH, and steam technologies at Launch Complex 34

	ISCO	**SPH**	**Steam**
Pre-Demonstration			
Mass of Total TCE (kg)			
Contouring	6,122	11,313	10,435
Kriging (80% CI)	6,217 to 9,182	7,498 to 15,677	11,145 to 14,159
Mass of TCE DNAPL (kg)			
Contouring	5,039	10,490	9,301
Post-Demonstration			
Mass of Total TCE (kg)			
Contouring	1,100	1,101	1,546
Kriging (80% CI)	1,511 to 2,345	1,031 to 1,535	1,328 to 2,540
Mass of TCE DNAPL (kg)			
Contouring	810	338	984
Cleanup Efficiency for Total TCE (%)			
Contouring	82	90	85
Kriging (80% CI)	62 to 84	80 to 93	80 to 90
Cleanup Efficiency for TCE DNAPL (%)			
Contouring	84	97	89

CI = Confidence Interval

Table 2: Amount (volume and mass of the aqueous solution) of $KMnO_4$ injected into the lithologic units each phase of treatment

Injection Phase	**USU**	**MFGU**	**LSU**			
	Volume (m^3)	**Mass of $KMnO_4$ (kg)**	**Volume (m^3)**	**Mass of $KMnO_4$ (kg)**	**Volume (m^3)**	**Mass of $KMnO_4$ (kg)**
Phase 1	325	6,059	353	8,484	476	13,904
Phase 2	249	4,923	82	1,348	-	-
Phase 3	165	3,372	225	4,589	1,316	24,277

Table 3: Cost summary of technologies

Technology	**Cost ($US)**	
	Per kg of TCE Removed or Destroyed[a)]	**Per m^3 of Geologic Media Treated[b)]**
ISCO	$224	$265
SPH	$64	$152
Steam Injection	$134	$283

a) Costs are based on the expense of treating the total estimated mass of TCE in each cell as calculated by the contouring method (see Table 1).

b) Costs are assumed to include treating contamination located within the footprint of the cell (15.2m x 22.9m) and extending over a depth range from 1.5m to 13.7m below ground surface (saturated zone). The total volume treated is ~4,250 m^3.

Figure 1: Location of treatment cells at Launch Complex 34. The total depth of treatment was approximately 13.7 m. Part of the volume treated underlies the Engineering Support Building.

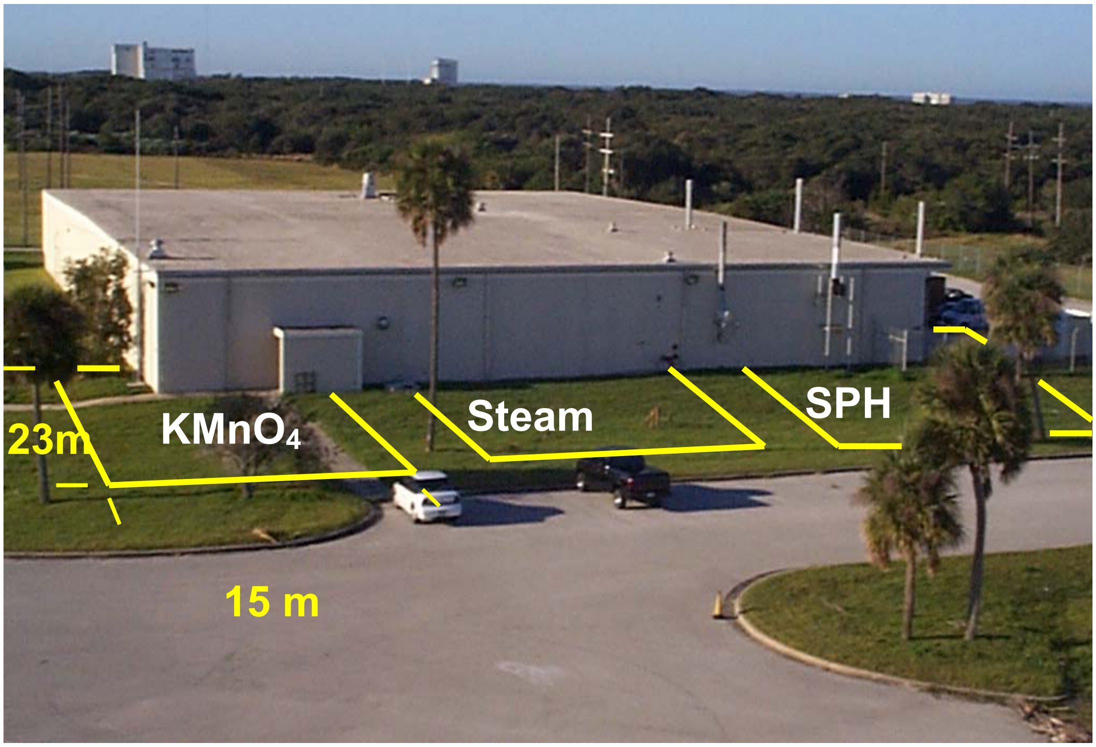
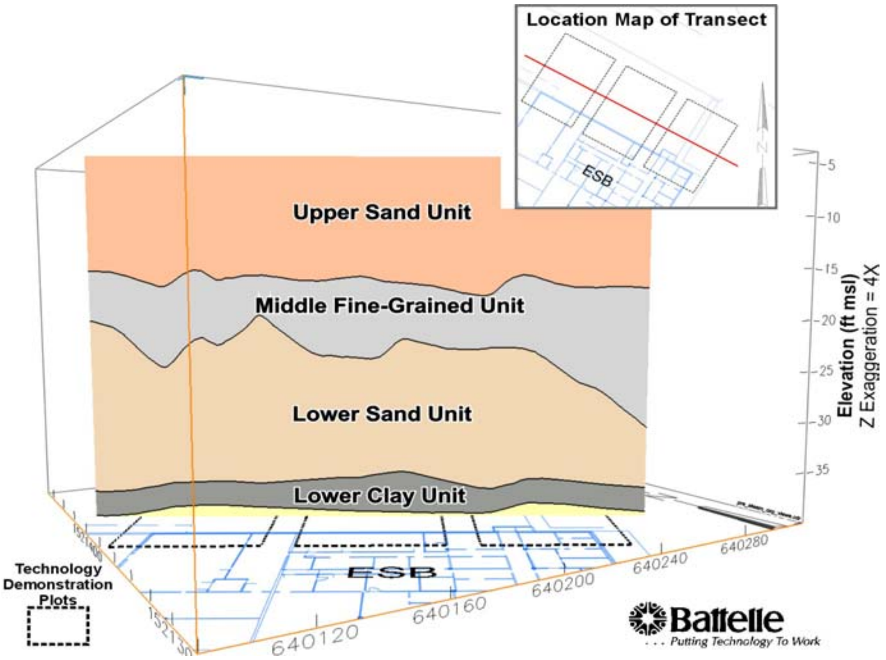


Figure 2: Lithologic cross section through the treatment cells. The Lower Clay Unit is a confining layer and represents the depth limit of treatment.



Project No. 21

Development and Use of a Permeable Adsorptive Reactive Barrier System for Ground Water Cleanup at a Chromium-Contaminated Site

Location	**Project Status**	**Contaminants**	**Technology Type**
Wood impregnation plant Leisi, Willisau, canton Luzern, Switzerland		Chromium (CrVI)	Permeable reactive wall
Technical Contact	**Project Dates**	**Media**	
Prof. Rita Hermanns Stengele Institute of Geotechnical Engineering Swiss Federal Institute of Technology Zurich CH-8093 Zurich, Switzerland Tel: +41-1-6662524 Fax: +41-1-6331248 E-mail: hermanns@igt.baug.ethz.ch	Accepted 2000	Ground water	
	Costs Documented?	**Project Size**	**Results Available?**
	Yes (estimated)	Full-scale	No

The information in this project summary is current as of January 2000.

1. INTRODUCTION

This on-site remediation project will be conducted at an ongoing wood impregnation plant in Willisau, a small village in the canton of Luzern, Switzerland. The downstream plume of chromium (CrVI) contaminated ground water will be treated by an innovative permeable adsorptive reactive barrier (PRB) system. A full-scale field installation will be conducted to clean up the contaminated ground water. Laboratory tests are running to evaluate the appropriate adsorptive filler material (no zero-valent iron). Project objectives are to learn about the long-term efficiency of the wall system regarding the geochemical/physical aspects, as well as the mechanical aspects.

2. BACKGROUND

The wood impregnation plant has existed since the beginning of the 20th century. It is located in the small village of Willisau in the canton of Luzern, Switzerland. The area is about 20,000 m2. Site investigation showed a main contamination with chromium in the soil and in the ground water due to the impregnation work, the handling, and, in the main case, the dump of impregnated wood on the unpaved terrain without any cover against rainfall.

Downstream from the plant area, the ground water is collected in a pumping station. The main contaminant in the ground water is chromium (CrVI) with a concentration ten times more than allowed in the Ordinance relating to the cleanup of contaminated sites (1998) in Switzerland.

The aquifer is about 10 m thick; the ground water level about 10 m under the surface. That means a permeable reactive barrier system of about 20 m depth has to be installed. The permeability of the aquifer is about $k_f \approx 10^{-3} - 10^{-4}$ m/s.

The project is funded by the Swiss Agency for the Environment, Forests and Landscape (50%). The other project partners are: Institute of Geotechnical Engineering, Swiss Federal Institute of Technology, Zurich; Dr. Franz Schenker, Geological Consulting, Meggen; BATIGROUP AG, construction company, Zurich and Ulrich Leisi, Willisau (owner of the plant), (all together 50%).

3. TECHNICAL CONCEPT

In the initial stage of the project, appropriate adsorptive filler (e.g., clay, bentonite, modified clay, or bentonite, zeolite) will be evaluated in the laboratory. They will be characterised based on mineralogy (e.g., x-ray, BET surface, exchange capacity). Following the selection of suitable materials, various mixes of reactive and filler materials will be prepared. This mixture will be tested regarding its effectiveness to reduce the contaminants, as well as regarding its mechanical behaviour and stability. Soil mechanical tests (e.g., permeability tests, erosion tests, and compressive strength tests) will be carried out. Batch and column tests will be used to measure parameters like adsorption capacity, time of reaction, and by-products.

At the same time, field data from the plant, especially regarding geology and hydrogeology, will be collected. Depending on the results, the ground water flow and contaminant transport will be modeled using a simulation system. The design of the reactive wall or the funnel-and-gate system (e.g., length, depth, and number of gates) also will be calculated using flow and transport modeling.

After finishing the laboratory tests, the PRB will be installed in the field. The construction of the PRB with the chosen suitable material for underground conditions will be tested in situ. The field results obtained will be compared with both the laboratory and numerical values. During the field installation careful performance monitoring is required. Parameters requiring monitoring to assess performance include: contaminant concentration and distribution, presence of possible by-products and reaction intermediates, ground water conductivity and ground water levels, permeability of the PRB, and ground water quality. Monitoring wells will be installed on both sides (upgradient and downgradient) of the wall in order to obtain information about remediation of contaminants and of the long-term performance (long-term monitoring).

4. ANALYTICAL APPROACH

Mineralogical composition will be determined using x-ray diffraction, BET surface area measurements with nitrogen, exchange capacity, and porosity. Pore size distribution will be determined with mercury pressure porosimetry and adsorption characteristics with water isotherms.

Chemical analysis depending on type of contaminant (e.g., atom adsorption spectometry or infrared spectometry) will be conducted.

Soil mechanical parameters will be determined using Swiss Standard Tests (e.g., compressive strength by unconfined compression strength tests, stress and deformation behaviour by oedometer tests, time-settlement behaviour (consolidation) by oedometer tests, friction angle and cohesion by direct shear tests, permeability tests with triaxial permeability cells).

5. RESULTS

The project started in summer 2000. Laboratory tests are running to evaluate appropriate adsorptive filler materials. There are no final results available at the moment. The installation of the PRB will start in autumn/winter 2001. The performance will be evaluated in the following months and years by monitoring the ground water quality, the remaining adsorption capacity of the filler material, and the functioning of the whole wall system.

The results of the project will be presented in half-year periods to the Swiss Agency for the Environment, Forests and Landscape and to all persons involved.

6. HEALTH AND SAFETY

During the installation of the PRB, no volatile substances will be released because no volatile contaminants were measured in the water or in the soil.
To avoid direct contact with heavy metals during excavation of soil and installation of the PRB, suitable coveralls, shoes, and gloves had to be worn by the manual workers.

7. ENVIRONMENTAL IMPACTS

An emission of volatile substances will not occur because of the above-mentioned types of contaminants. To avoid an unacceptable noise level during the installation of the PRB, the Swiss Regulations will be followed.

Pumped water will be analysed and, in the case of contamination, sent to a treatment plant.

8. COSTS

In the very early stages of this project, the cost was estimated about sfr. 1.3M (about U.S.$ 0.8M). Specific costs will be reported at a later date.

9. CONCLUSIONS

The objective of this research project is the development of a novel adsorptive media to apply in PRBs for ground water cleanup at a chromium-contaminated site. Geochemical and soil mechanical tests are currently being conducted. Laboratory test results should be applied and verified by implementing field tests.

As soon as suitable, the permeable adsorptive reactive barrier system should be verified in full-scale at the chromium contaminated wood impregnation plant in Willisau. During and after installation of the PRB, a monitoring concept has to be carried out to verify the long-term behaviour of the reactive wall, as well as the ground water contamination.

10. REFERENCES

1. EPA United States Environmental Protection Agency: Field Applications of in situ Remediation Technologies: Permeable Reactive Barriers. In EPA 542–R–99–002, 1999.

2. Gavaskar, A.R.; Gupta, N.; Sass, B.M.; Janosy, R.J. & O'Sullivan, D.: Permeable Barriers for Groundwater Remediation. Design, Construction and Monitoring. Ohio: Batelle Press Columbus, 1998.

3. Köhler, S. and Hermanns Stengele, R.: Permeable Reactive Barrier Systems for Groundwater Cleanup. GeoEng 2000. International Conference on Geotechnical & Geological Engineering, Melbourne: (in print) 2000

Project No. 22

Thermal In-situ Remediation of the Unsaturated Zone by Steam Injection

Location	**Project Status**	**Contaminants**	**Technology Type**
Former hazardous waste disposal site, Mühlacker, Germany	Finished	TCE, BTEX	Steam injection
Technical Contact Dr.-Ing. H.-P. Koschitzky Dipl.-Ing. T. Theurer Research Facility for Subsurface Remediation, VEGAS University of Stuttgart Pfaffenwaldring 61 D-70569 Stuttgart, Germany E-mail: hans-peter.koschitzky@iws.uni-stuttgart.de	**Project Dates** July 1999-November 2001	**Media** Unsaturated zone	
	Costs Documented? yes	**Project Size** Pilot-scale	**Results Available?** yes

Project 22 was completed in 2001.

1. INTRODUCTION

Combined steam injection and soil vapour extraction can accelerate and improve the clean-up of contaminated unsaturated soils due to significant changes in contaminant properties with increasing temperature. The main effect is the dramatic increase in contaminant vapour pressures leading to high removal rates in the vapour phase.

A pilot scale demonstration project using this technology has been carried out at a former hazardous waste disposal site near the town of Mühlacker in southwestern Germany.

2. BACKGROUND

In the late 1960s a disposal site for hazardous wastes containing chlorinated solvents and galvanic sludges was opened in a forest near Mühlacker. The wastes were deposited within a layer of silty loam, which was considered to be impermeable enough to protect the subsurface underneath from being contaminated by the leachate of the waste site. Nevertheless, by the late 1970s, contaminants had migrated through the unsaturated zone, below which consists of highly heterogeneous weathered sandy marl and were detected in the underlying keuper gypsum aquifer 30 m below ground surface. Detailed site investigation lead to the conclusion that separate phase contaminants (mainly TCE) were retained by a capillary barrier intersecting the unsaturated zone at a depth of 15 m below ground surface.

Soon after that the site was included in the model site program ("Modellvorhaben") funded by the state of Baden-Württemberg and remediation activities started. The site was encapsulated by sheet piles and an asphalt cover was placed on the surface to reduce the leachate flux from the deposited waste. Remediation of the deposited waste itself and the groundwater zone was conducted as well as conventional soil vapour extraction in the unsaturated zone. Due to the complex nature of the subsurface, in-situ remediation of the unsaturated zone by means of conventional methods was ineffective. To enhance contaminant removal a thermally enhanced remediation scheme was installed in a section of the site where steam can be injected in the highly contaminated zone between 7 and 15 m below ground surface. The total volume of soil to be treated in the target area is approximately 3000 m^3.

The pilot plant was operated by the two companies Züblin Umwelttechnik GmbH and Preussag Wassertechnik GmbH and *VEGAS* from the University of Stuttgart, who conducted the scientific oversight. The pilot study was funded by the "Kommunaler Altlastenfonds" and the city of Mühlacker, represented by the consultant company Weber-Ingenieure GmbH.

3. TECHNICAL CONCEPT

The egg-shaped test field with a diameter of about 20 m consisted of one central steam injection well surrounded by six extraction wells. The extraction wells could be used simultaneously for vapour and liquid extraction. All wells reached to a depth of 16 m below ground surface and were screened from 7 m to 15 m. Steam was generated using a gas-fired 110 kW steam generator. Extracted gases were passed through a condenser. Incondensable gases were passed through a catalytic combustion unit before being vented to the surrounding atmosphere. Condensate was passed through liquid separators where the contaminant was separated from the water. Liquids were removed from the wells with surge pumps, passed through a cooler and passed through a separator to seperate the non-aqueous phase (NAPL) from the water.

In order to measure temperatures in the subsurface up to a depth of 15 m, ten temperature monitoring lances were installed with a total of 100 sensors spaced every 70 cm of depth. Detailed monitoring of gas and liquid flow rates and temperatures was carried out during the pilot test.

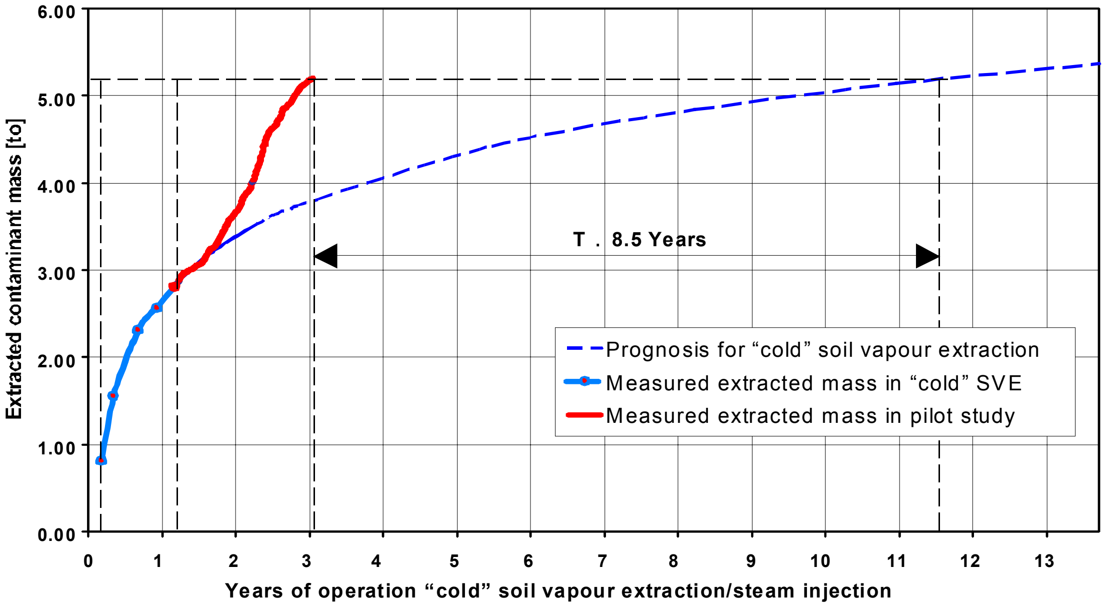
4. ANALYTICAL APPROACH

Soil samples were taken and analyzed to determine the extend of subsurface contamination. For this purpose contaminants were extracted from the soil by a solvent and analyzed using the HPLC method. During operation, contaminant concentrations were measured regularly in the extracted vapours and liquids using GC and HPLC methods and a flame ionization detector (FID).

5. RESULTS

After a total of ten months of steam injection, almost complete heating of the target zone has been achieved. The problem of the steam front being displaced by the high water content of the soil material could be overcome by filtering the water particles out of the injected steam. Intermittent steam injection was used to reach a more uniform temperature distribution in the subsurface. Since the completion of the steam injection in March 2001, the test field has been cooling. Altogether, 2800 kgs of TCE have been removed, of which about 95% were extracted in the gaseous phase and the remaining part as solute in condensed water.

Figure 1: Mass output performance in steam injection pilot study compared to cold soil vapour extraction



The mass output performance of the pilot study is shown in Figure 1. At the field site, cold soil vapour extraction had been conducted for approx. one year before the pilot study, resulting in the high contaminant removal rate shown by the line with dots. However, at the beginning of the steam injection pilot study, performance had been decreased. The thermal treatment again raised the removal rate and kept it high during the steam injection. Compared with the period estimated for remediation with cold soil vapour extraction (dashed line), steam injection meant a saving of 8.5 years.

Estimating the performance of cold soil vapour extraction to be expected (dashed line), the conclusion that steam injection resulted in a time saving of 8,5 years for remediation can be drawn.

The project was finished and accounted for end of September, 2001. The cooling process, however, is expected to continue approximately until the end of 2002. Subsurface temperatures will be measured frequently in longer intervals to survey the cooling process.

6. HEALTH AND SAFETY

Safety equipment was used by the staff according to German safety regulations. The pilot plant was equipped with warning systems to control vapour and liquid streams, temperatures and performance of the pumps.

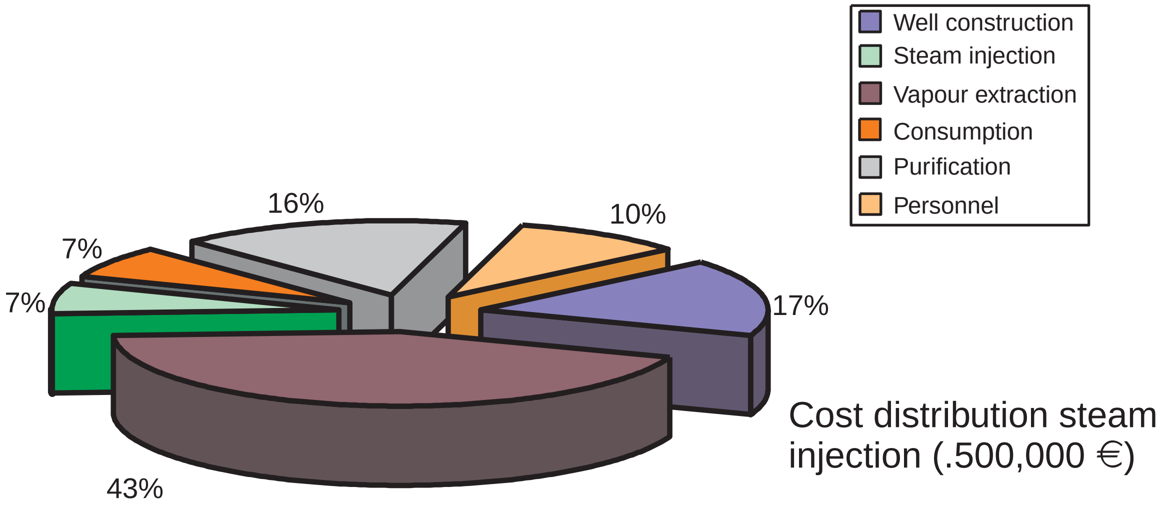
7. ENVIRONMENTAL IMPACTS

Extracted vapours and liquids were cleaned on-site in a treatment facility consisting of a catalytic combustion unit and stripping columns. Thus, emissions to the environment were entirely avoided. Measures for protection against noise were undertaken. Wells were installed to monitor contaminant concentrations in the underlying aquifer in order to be able to take interactive measures in the case of a possible mobilisation of DNAPL.

8. COSTS

The costs for the cleanup of the extracted soil air could only be determined theoretically because, at the field site, the cleaning was coupled to a large plant for groundwater and cold soil vapour extraction and it was not possible to calculate the costs of the pilot study alone.

Figure 2: The cost and cost distribution of steam injection pilot study



Expenses of about 200,-€ per cubic meter and approximately 190,- € per kilogram of extracted TCE were estimated.

Figure 2 shows the cost distribution of the pilot study. By far the highest expenses were incured by the costly soil vapour extraction plant, which must be fitted for hot gases and treatment of different phases. Energy consumption accounted for only a small fraction. The cost of cold soil vapour extraction calculated for the whole remediation period (see Figure 1) would have been 50% higher than that of the pilot study.

9. CONCLUSIONS

Despite the low permeability of the subsurface, steam injection could be applied successfully. The problem of the buoyancy of the heat front because of capillary water in the subsurface could be overcome by ensuring only a very low water input. Use of intermittent steam injection towards the end of the heating process led to a more uniform temperature distribution. Conductive heat transport in injection breaks warmed up regions of the soil where convective heat transport was negligible.

10. REFERENCES

1. Koschitzky, H.-P., Theurer, T., Schmidt, R., Winkler, A., Färber, A. (2000): Pilot-scale study of steam injection for thermal in-situ remediation of the unsaturated zone below a hazardous waste site. Proc. ConSoil2000, Leipzig

2. Koschitzky, H.-P., Theurer, T., Schmidt, R., Winkler, A., Färber, A. (2000b): In situ remediation of unsaturated zone by steam injection: results of pilot studies. Proc. „Implementation of in-situ remediation techniques: Chlorinated solvents and heavy metals“, Utrecht

3. Koschitzky, H.-P., Theurer, T., Färber, A. (2001): Einsatz des thermischen In-situ-Sanierungsverfahrens TUBA unter schwierigen Bedingungen. Boden und Altlasten-Symposium, Berlin 21.02.-22.02. 2001 (in German)

4. Schmidt, R., Koschitzky, H.-P. (1999): Pilothafte Sanierung eines BTEX Schadens an einem ehemaligen Gaswerksstandort mit der thermisch unterstützten Bodenluftabsaugung (TUBA) durch Dampfinjektion, Wiss. Bericht WB 99/5 (HG 262), Institut für Wasserbau, Universität Stuttgart (in German).

5. Theurer, T., Winkler, A., Koschitzky, H.-P. & Schmidt, R. (2000): Remediation of a landfill contamination by steam injection. In: Groundwater 2000, Proc. of the Intl. Conference on Groundwater Research, Copenhagen, Denmark, 6-8 June 2000, 371-372.

6. Theurer, T., Koschitzky, H.-P., Färber, A. (2001): Modellvorhaben Mühlacker: Modellhafte In-situ-Sanierung durch Dampfinjektion nach dem TUBA-Verfahren. Technischer Bericht 2001/03 (HG 280), Institut für Wasserbau, Universität Stuttgart (in German).

Project No. 23

Bioremediation of Pesticides7

Location Stauffer Management Company Superfund Site, Tampa, FL	**Project Status** Completed Project	**Contaminants** Chlordane, DDT, DDD, DDE, dieldrin, molinate, toxaphene	**Technology Type** Composting process (Xenorem TM)
Technical Contact Brad Jackson U.S. EPA, Region 4 61 Forsyth Street, SW Atlanta, GA 30303-8960 Tel: 404-562-8925 Fax: 404-562-8896 Neil C.C. Gray, Ph.D. AstraZeneca Canada 2101 Hadwen Road Mississauga, Ontario L5K 2L3 Tel: 905-403-2748 Fax: 905-823-0047 E-mail: neil.gray@astrazeneca.com	**Project Dates** Accepted 2000 Final Report 2001	**Media** Soil and pond sediments	
	Costs Documented? Yes, for both field demonstration and full-scale operations	**Project Size** Field Demonstration: 500 yd3 Full-scale: 8,000 yd3 Full-scale: 16,000 yd3 in 4,000 yd3 batches	**Results Available?** Yes, for both field demonstration and full-scale operations

Project 23 was completed in 2001.

1. INTRODUCTION

The Stauffer Management Company (SMC) Tampa site is one among a small number of U.S. contaminated waste sites implementing bioremediation at full-scale to cleanup soils with pesticide contamination. A completed field demonstration (500 yd^3) using soil contaminated with high levels of DDT showed that the DDT could be biodegraded without the end accumulation of the major metabolites, DDD and DDE. In comparison, DDT was readily degradable, so was the more recalcitrant metabolites; a reduction of more than 90 percent for DDD occurred.

Beginning in May 2000, the project has been operating under full-scale conditions at the SMC Tampa site, with 4,000 yd^3 of contaminated soil being treated in each batch.

In addition to the operation at the SMC site, 8,000 yd^3 of pesticide contaminated soil (with high levels of toxaphene) from the Helena Chemical superfund site (Tampa, FL) was also excavated and successfully treated using this technology; this project was finished in early 2001.

2. BACKGROUND

Located in Tampa, Florida, the SMC site formulated and distributed agricultural chemical products (organochlorine, thiocarbamate and organophorphorus pesticides) from 1951 to 1986. Up to 1973, waste materials from the facility were disposed of on site by two methods: burial or incineration. The containerized wastes, packaging materials, and other pesticides buried led to pesticide contamination in soil, surface water, and sediment in on site ponds and in groundwater underlying the site.
The site received final status under the Superfund program in 1996. Thermal desorption was initially chosen as the remedial option. However, due to high sulfur and other compounds in the soil, the implementation of thermal desorption was determined to be unsafe for the SMC site. Therefore, bioremediation was identified as the selected remedy for the pesticide-contaminated surface soils and sediments at the site.

The objective of the laboratory research trials and the field demonstration was to determine if the composting process could meet the specified cleanup levels or achieve 90 percent reduction in contaminant concentration. These objectives were met, leading to the implementation of bioremediation as the full-scale technology for the site.

3. TECHNICAL CONCEPT

AstraZeneca Canada, an affiliated company of SMC, developed a patented enhanced composting process called XenoremTM for remediating soils contaminated with recalcitrant organics, such as chlorinated pesticides, PAHs and explosives. XenoremTM uses anaerobic and aerobic cycles to bioremediate the parent compound and daughter products of concern. Laboratory studies (e.g. radio-labeled biodegradation studies, fate studies, microbial screening etc.), were followed by comparative lab and pilot studies (14, 60, and 100 yd^3), and a field study (500 yd^3), before moving to full-scale operations. A number of engineering configurations were also comparatively evaluated in the field, including landfarming, biopiles, and composting in order to evaluate the Xenorem^{TM} technology.

Organic amendments are added to the contaminated soil to enhance the temperature within the pile and to aid in creating the anaerobic periods. Aerobic periods were created by mechanical mixing, using a SCAT windrow turner. The indigenous microflora associated with the contaminated soil is manipulated by changing the environment associated with the soil matrix. Based on a decision tree, created from the results of microcosm and respirometry studies, the duration and degree of each of the anaerobic/aerobic cycles is predetermined.

For the first 4,000 yd^3 batch, the soil was excavated, screened, mixed and amended with dairy manure, wood chips and chicken litter. The amended soil matrix was engineered into a compost windrow, built inside a Big Top structure. Due to potential odor issues from some of the pesticides, and the high groundwater table in the area, it was prudent to carryout the operation in an enclosure. An odor abatement system, consisting of two blowers, four particulate prefilters and a 10 ton carbon charge to polish the air stream was used.

4. ANALYTICAL APPROACH

To monitor the progress in the full-scale operation, eight composite samples were collected from the windrow, on a regular basis (e.g. after an anaerobic/aerobic cycle); the seven chemicals of concern, as listed in the record of decision for the site, were chlordane, DDD, DDE, DDT, dieldrin, molinate and toxaphene. At time-zero (T0) and at the end of the run (Tf), 40 composite samples were taken. The soil samples were analyzed using EPA Method 8081A. For toxaphene analysis, gel permeation chromatography (SW846 Method 3640A) and sulfuric acid (based on SW846 Method 3665A) clean-up methods were performed on the soil samples prior to chemical analysis by EPA Method 8081A.

The environmental parameters (temperature, redox, oxygen, and moisture levels) were monitored continuously using a data acquisition/controller system, permitting real-time access to the data. Measurement confirmation was also carried out using hand-held probes.

5. RESULTS

Tables 1 and 2 show the cleanup levels specified for selected constituents, the initial (T0) and end (Tf) concentrations for the field trial and full-scale operation, and the percent reduction in concentration over that period.

Table 1: Summary of End-Points Achieved for the 500 yd^3 Field Trial

Pesticide	ROD Level (ppm)	To Value (ppm)	Tf Value (ppm)	% Degraded	Comments
Chlordane	2.3	47.5	5.2	89	Ca. 90%
DDD	12.6	242	23.1	90.5	>90%
DDE	8.91	11.3	6.8	40	ROD
DDT	8.91	88.4	1.2	98	ROD
Dieldrin	0.19	3.1	<MDL	<MDL	<MDL
Molinate	0.74	10.2	<MDL	<MDL	<MDL
Toxaphene	2.75	469	29	94	>90%

Table 2: Summary of End-Points Achieved for the 4,000 yd^3 Full-scale Operation

Pesticide	ROD Level (ppm)	To Value (ppm)	Tf Value (ppm)	% Degraded	Comments
Chlordane	2.3	3.8	<MDL	<MDL	ROD
DDD	12.6	26	9.3	65	ROD
DDE	8.91	6.6	2.1	68	ROD
DDT	8.91	82	9.8	88	ROD
Dieldrin	0.19	2.4	<MDL	<MDL	ROD
Molinate	0.74	0.2	<MDL	<MDL	ROD
Toxaphene	2.75	129	7.8	94	>94%

6. HEALTH AND SAFETY

A complete Work Plan, including a Site Specific Health and Safety Plan was followed for both the field trial as well as for the full-scale operation. Air monitoring was carried out during all soil handling operations, with no excursions over the action limits cited.

It should be noted that if the soil contains high levels of sulfur, the production of hydrogen sulfide could occur.

7. ENVIRONMENTAL IMPACTS

No environmental impacts were found. Once the soil is treated, it is available to be used as fill at the site.

8. COSTS

For the full-scale operation (4,000 yd^3 batch) the total project costs were estimated at \$192/yd^3, including \$132/yd^3 for the treatment using XenoremTM; this cost can be significantly reduced if the work is carried out by the owner of the site, if the amendments used are local and if the operation is greater in scale. Regulatory requirements and/or the end point that has to be achieved also influence the costing.

9. CONCLUSIONS

Data collected in the field trial, the full-scale operation, and the previous laboratory and pilot-scale work demonstrated that the ROD chemicals of concern are biodegradable. The Xenorem^{TM} technology, when operating within the optimal environmental/process windows is effective in reducing the target pesticides to the ROD levels and/or at least 90%, for the SMC Tampa site.

It has been demonstrated that the field conditions can be manipulated/controlled to provide/create the necessary conditions for the technology to work successfully. As additional data and "learning curve" experiences are evaluated, the operational parameters for each new batch are being modified, to increase the overall efficiency of the operation.

10. REFERENCES

1. Gray, N.C.C., P.R. Cline, A.L. Gray, L.E. Moser, G.P. Moser, H.A. Guiler, B. Boyd and D.J. Gannon, 2001. Full-scale soil bioremediation of chlorinated pesticides. 6th In Situ and On-Site Bioremediation International Symposium, San Diego, CA. June 4th-7th.

2. Gray, N.C.C., P.R. Cline, A.L. Gray, L.E. Moser, G.P. Moser, H.A. Guiler, B. Boyd and D.J. Gannon, 2000. Bioremediation of DDT and toxaphene contaminated soils. 16th Annual International Conference on Contaminated Soils, Sediments and Water, Amherst, MA, October 16th.

3. Gray, N.C.C., P.R. Cline, A.L. Gray, L.E. Moser, G.P. Moser, H.A. Guiler, B. Boyd, and D.J. Gannon, 2000. Anaerobic/aerobic cycling to bioremediate pesticide contaminated soils. 6th International Conference on Advanced Oxidation Technologies for Water and Air Remediation, London, Ontario, June 25-30th.

4. Gray, N.C.C., P.R. Cline, G.P. Moser and D.J. Gannon, 2000. Bioremediation of toxaphene contaminated soil. Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds. Monterey, CA. May 24th.

5. Gray, N.C.C., 2000. Full-scale bioremediation of chlorinated pesticides, Biotech Mag, April edition

6. Moser, G.P., N.C.C. Gray and D.J. Gannon, 2000. Treatment of nitroaromatic contaminated soils using the Xenorem technology. Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA. May 23rd.

7. U.S. Environmental Protection Agency, 2000. Cost and Performance Report: Bioremediation at the Stauffer Management Company Superfund Site, Tampa, Florida.

8. Moser, G.P., N.C.C. Gray and D.J. Gannon. 2000. Compost Decontamination of Soil Contaminated with Polychlorinated Biphenyls Using Aerobic and Anaerobic Microorganisms. U.S. Patent No. 6,083,738 (July 4th).

9. Moser, G.P. and N.C.C. Gray. 2000. Compost Decontamination of Soil Contaminated with Pentachlorophenol Using Aerobic and Anaerobic Microorganisms. U.S. Patent No. 6,033,899 (March 7th).

10. Moser, G.P., N.C.C. Gray and D.J. Gannon, 2000. Compost Decontamination of Soil Contaminated with Polychlorinated Biphenyls using Aerobic and Anaerobic Microorganisms. U.S. Patent No. 6,083,738 (July 13th).

11. Moser, G.P. and N.C.C. Gray, 1999. Compost Decontamination of Soil Contaminated with TNT, HMX, and RDX with Aerobic and Anaerobic Microorganisms. U.S. Patent Number: 5,998,199 (December 7th).

12. Gray, N.C.C., G.P. Moser and L.E. Moser, 1999. Compost Decontamination of Soil Contaminated with Chlorinated Toxicants. U.S. Patent Number 5,902,744 (May 11th).

13. Bernier, R.L., N.C.C. Gray and A.L. Gray, 1997. Anaerobic/aerobic Decontamination of DDT Contaminated Soil by Repeated Anaerobic/Aerobic Treatments. U.S. Patent Number: 5,660,613 (August 26th).

14. Bernier, R.L., N.C.C. Gray and L.E. Moser, 1997. Compost Decontamination of DDT Contaminated Soil. U.S. Patent Number: 5,660,612 (August 26th).

Project No. 24

Surfactant-Enhanced Aquifer Remediation

Location Site 88, Marine Corps Base, Camp Lejeune, NC	**Project Status** Completed Project	**Contaminants** Tetrachloroethylene (PCE)	**Technology Type** Surfactant flushing
Technical Contacts Laura Yeh Naval Facilities Engineering Service Center 1100 23rd Ave. Port Hueneme, CA 93043 Tel: 805-982-1660 Fax: 805-982-1592 E-mail: yehsl@nfesc.navy.mil Leland M. Vane, Ph.D. U.S. EPA National Risk Management Research Laboratory 26 W. Martin Luther King Dr. Cincinnati, OH 45268 Tel: 519-569-7799 Fax: 513-569-7677 E-mail: vane.leland@epa.gov Gary A. Pope, Ph.D. The University of Texas Austin, TX 78712 Tel: 512-471-3235 Fax: 512-471-3605 E-mail: gpope@mail.utexas.edu Frederick J. Holzmer Duke Engineering & Services 4433 NW Seneca Ct. Camas, WA 98607 Tel: 360-834-6352 Fax: 360-834-7003 E-mail: fjholzme@dukeengineering.com	**Project Dates** Accepted 2000 Final Report 2001	**Media** Groundwater	
	Costs Documented? Yes	**Project Size** Field Demonstration (wellfield size of 20 feet by 30 feet)	**Results Available?** Yes

Project 24 was completed in 2001.

1. INTRODUCTION

Surfactant flushing offers the potential to address hazardous waste sites contaminated with non-aqueous phase liquids (NAPL) in groundwater. A field demonstration of surfactant enhanced aquifer remediation (SEAR) was conducted for dense-NAPL (DNAPL) remediation at the Marine Corps Base (MCB) Camp Lejeune Superfund Site. The project was the first field demonstration to implement surfactant recycling (i.e., surfactant recovery and reinjection) in the United States.

2. BACKGROUND

A PCE-DNAPL zone was identified and delineated at the central dry cleaning facility, known as Site 88, at the MCB Camp Lejeune, North Carolina. Discovered by extensive soil sampling in 1997, the site was further characterized by a partitioning interwell tracer test (PITT) in 1998.

The DNAPL zone is located in a shallow aquifer beneath the dry cleaning facility at a depth of approximately 17 to 20 feet below ground surface (bgs). A thick clay aquitard is present at about 20 feet bgs, which has effectively prevented further downward DNAPL migration at this site. The shallow aquifer is characterized as a relatively low-permeability formation composed of fine to very-fine sand, with a fining downward sequence in the bottom two feet of the aquifer. The bottom, fine-grained zone, referred to as the basal silt layer, grades to silt then clayey silt before contacting the aquitard. Permeability decreases downward through the basal silt layer as a function of decreasing grain size with depth.

DNAPL was present in the test zone as free-phase and residual DNAPL in the fine sand and basal silt. Recovery of free-phase DNAPL was undertaken before the PITT by conventional pumping and water flooding. The pre-surfactant PITT measured approximately 74-88 gallons of PCE in the test zone. The average DNAPL saturation estimated by the PITT was approximately 4 percent near the dry-cleaning building and decreased to about 0.4 percent at a distance of about 15 to 20 feet from the building.

A field demonstration of surfactant-enhanced aquifer remediation (SEAR) was conducted at Site 88 during the spring of 1999. The objectives of the field demonstration were to: (1) validate in situ surfactant flooding for DNAPL removal; (2) promote the effective use of surfactants for widespread DNAPL removal; (3) demonstrate that surfactants can be recovered and reused; and (4) show that surfactant recycle can significantly reduce the overall cost of applying surfactants for subsurface remediation.

3. TECHNICAL CONCEPT

The plan-view footprint of the SEAR demonstration well field was 20 feet by 30 feet. The SEAR demonstration was conducted during April to August 1999, with a 58-day surfactant flood and followed by a 74-day water flood. The demonstration utilized a custom surfactant, Alfoterra 145 4-PO sulfate™, which was developed for the dual objectives of high PCE solubilization and desirable effluent treatment properties (for surfactant recovery and reuse).

During the surfactant injection period, the extraction well effluent was treated using two membrane-based processes to first remove the contaminant and then to reconcentrate the surfactant for reinjection. Pervaporation was used to remove PCE from the extraction well effluent while micellar enhanced ultrafiltration (MEUF) was employed to recover the surfactant. Regulations by the state of NC required 95 percent contaminant removal prior to surfactant reinjection. The pervaporation system removed 99.94 percent of the PCE from groundwater in the absence of surfactant and 95.8 percent PCE during periods of peak surfactant concentrations. The MEUF system concentrated the surfactant from < 1 percent by weight (wt %) in the extraction well effluent to 5 wt%, slightly above the reinjection concentration of 4 wt%. Recovered surfactant was reinjected into the contaminated aquifer for the final 18 days of the surfactant flood, thereby demonstrating the technical and regulatory feasibility of recovering and reusing surfactants for aquifer remediation projects.

4. ANALYTICAL APPROACH

Monitoring included the regular collection of samples for analysis, in accordance with the sampling and analysis plan. System operations also were continually monitored according to the work plan. Likewise, the analytical methods used to monitor and assess the SEAR performance can be found in the sampling and analysis plan.

5. RESULTS

A total of 76 gallons of PCE was recovered during the surfactant flood and subsequent water flood, of which approximately 32 gallons of PCE were recovered as solubilized DNAPL and 44 gallons were recovered as mobilized free-phase DNAPL. Performance assessment of the demonstration is based upon the analysis of 60 soil core samples that were collected at the completion of the SEAR demonstration. Continuous soil cores were collected from approximately 17-20 ft bgs and field preserved with methanol. Soil core data analysis estimated that a total of 29±7 gallons of DNAPL remains in the test zone following the surfactant flood, distributed between the upper zone (fine sand sediments) and the lower zone (basal silt layer).

Post-SEAR soil core data was further analyzed by subdividing the data into the upper and lower zones to evaluate the effects of decreasing permeability upon the post-SEAR DNAPL distribution. The results indicate that approximately 5 gallons of DNAPL remains in the upper zone, i.e., equivalent to about 92-96 percent removal from the upper zone, and approximately 24 gallons of the DNAPL is estimated to remain in the lower zone, which was relatively unaffected by the surfactant flood. Effective DNAPL recovery from the lower zone was limited by the permeability contrast between the upper fine sand zone and the low-permeability basal silt layer. Hydraulic conductivity (K) in the upper zone is estimated to be on the order of about 1×10^{-4} to 5×10^{-4} cm/sec (0.28 – 1.4 ft/day), whereas K in the basal silt is estimated to be as low as about 1×10^{-5} to 1×10^{-4} cm/sec (0.028 - 0.28 ft/day), decreasing with depth to the aquitard.

Based on soil samples analyzed prior to the surfactant flood, the highest pre-SEAR DNAPL saturations occurred in the upper, more permeable zone. The upper zone is the primary transmissivity zone for transport of the dissolved-phase PCE plume at Camp Lejeune. Data analysis of post-SEAR DNAPL conditions indicates that greater than 92 percent of the source was removed from the upper, transmissive zone, and that the remaining DNAPL is relatively isolated in the basil silt layer (i.e., low-permeability zone). The flux of dissolved PCE, from dissolution of DNAPL in the lower zone, to the upper zone will be primarily limited to diffusion. Therefore, the source of the dissolved PCE plume is believed to be substantially mitigated compared to pre-SEAR conditions. The overall effect of the surfactant flood is that transport of the dissolved PCE plume from the SEAR treatment zone should be greatly reduced since the primary mechanism for plume generation is now largely limited to diffusion of dissolved PCE from the basal silt zone to the overlying transmissive zone. Details of this demonstration project can be found in the Final Technical Report (Battelle and Duke Engineering & Services, 2001a).

6. HEALTH AND SAFETY

No significant health and safety issues are associated with the implementation of SEAR, other than potential exposure to DNAPL from handling the DNAPL-laden wastewater.

7. ENVIRONMENTAL IMPACTS

Environmental impact concerns for surfactant flushing include: hydraulic containment and recovery of injected fluids, toxicity and biodegradability of the surfactant, and the potential risk associated with mobilizing DNAPL. The demonstration at Site 88 maintained effective hydraulic control and recovery of the injectate, with the exception of a minor loss of hydraulic control for a short period, followed by reestablishment of hydraulic control. The surfactant used at Camp Lejeune exhibits low toxicity and was biodegradable. DNAPL was mobilized, by design, during the demonstration. Downward migration by mobilized DNAPL was addressed as result of the thick aquitard present at the site.

8. COSTS

An evaluation of the costs associated with the demonstration, as well as estimated costs for a full-scale remediation at Camp Lejeune, can be found in the Cost and Performance Report for Surfactant Enhanced Aquifer Remediation (SEAR) Demonstration, Site 88, MCB Camp Lejeune, NC (Battelle and Duke

Engineering & Services, 2001b). The report also includes a comparison of costs for full-scale SEAR at a high-permeability site, as well as cost comparisons to alternative remedial technologies. The alternative technologies were compared only on a cost basis since there is no performance data for these technologies at Site 88, MCB Camp Lejeune. Under the majority of scenarios studied, contaminant removal followed by recovery and reuse of surfactant provided an overall cost savings. However, in all scenarios, the net effect on remediation cost of recovering and reusing surfactants was marginal.

9. CONCLUSIONS

Results from the project indicate greater than 92 percent removal from the upper portion of the treatment zone, which is the zone that contained the highest DNAPL saturations before conducting the demonstration. The DNAPL in the basal silt layer (i.e., low-permeability zone) was relatively unaffected by the surfactant flood. The SEAR demonstration targeted the removal of DNAPL from only approximately 25 percent of the entire DNAPL zone for Site 88. Therefore, the amount of reduction in the PCE plume as a result of the demonstration is difficult to confirm at this time unless the remainder of the DNAPL zone is remediated to a similar degree as the demonstration area.

10. REFERENCES

1. Battelle and Duke Engineering & Services, 2001a. "Final Technical Report for Surfactant-Enhanced DNAPL Removal at Site 88, Marine Corps Base Camp Lejeune, North Carolina." Prepared for NFESC by Battelle, Columbus, OH and Duke Engineering & Services, Austin, TX.

2. Battelle and Duke Engineering & Services, 2001b. "Final Cost and Performance Report for Surfactant Enhanced DNAPL Removal at Site 88, Marine Corps Base Camp Lejeune, North Carolina." Prepared for Naval Facilities Engineering Service Center (NFESC) by Battelle, Columbus, OH and Duke Engineering & Services, Austin, TX.

Project No. 25

Liquid Nitrogen Enhanced Remediation (LINER): A New Concept for the Stimulation of the Biological Degradation of Chlorinated Solvents

Location	**Project Status**	**Media**	**Technology Type**
The Netherlands	New project	Soil and groundwater	Substrate injection
Technical Contact Chris Schuren, Emile Marnette Tauw bv E-mail: chs@tauw.nl Gijsbert-Jan Groenendijk Hoek Loos bv	**Project Dates** February 2000- July 2003	**Contaminants** VOCls	
	Costs Documented?	**Project Size** Field demonstration	**Results Available?** Yes

The information in this project summary is current as of January 2002.

1. INTRODUCTION

One of the major problems involved in soil remediation today is the treatment of deep groundwater contaminated with chlorinated hydrocarbons. Biological degradation by microorganisms will often be the best clean-up option. In practice, however, the addition of the substrate required to stimulate the biological processes in-situ is a problem. Substrate infiltrated in liquid form mixes very slowly with the contaminated groundwater and infiltration systems tend to clog easily. Furthermore, the limited radius of influence of an infiltration well requires a dense network of wells.

In cooperation with gas company Hoek Loos, engineering consultancy Tauw has developed a new remediation concept, overcoming most of the limitations inherent to the conventional in-situ biological systems for degradation of CAH.

Remediation of soil contaminated with CAH. The Netherlands have numerous sites contaminated with CAH. The most common remediation approach concerns pump and treat. However, authorities frequently impose severe restrictions on groundwater extraction. In-situ air sparging based on the injection of compressed air (possibly in combination with techniques such as steam injection, electro reclamation etc.) may be an alternative for contaminants located in relatively shallow soil layers.

Over the past few years, methods to promote indigenous biological degradation of contaminations at greater depths have been developed: the bacterial population present is stimulated to biotransform CAH contamination. All methods involve introduction of a substrate (electron donor) into the subsurface.

Groundwater substrate transport. Substrate infiltrated in the subsurface as a liquid will mix very slowly with the ambient groundwater. Degradation will mainly occur at the interface of the infiltrated substrate and the contaminated groundwater. Infiltrated substrate flowing along with groundwater may be degraded before reaching other contaminated areas downstream. Consequently, the network of infiltration points required to effectively stimulate an existing natural attenuation processes will have to be very dense. The cost of such networks makes them practically unfeasible, particularly for contaminations located at large depths. Another potential problem involved in infiltration of substrates in liquid form is clogging of the wells by biomass formation.

LINER - Gas/substrate injection. The injection of a substrate with gas as a means for distribution is a concept, which has not yet been tested as a remediation technique. This method combines two concepts: stimulation of biodegradation of CAH by the addition of a substrate, and in-situ air sparging. Due to the anaerobic nature of the targeted microbiological processes, nitrogen gas was used instead of compressed air. The flow rate at which gas is distributed both horizontally and vertically within the soil is expected to be much higher than that of water, which should make the injection of gas a much more effective procedure than infiltration of an aqueous solution. Also, introducing substrate with a carrier gas is expected to result in a much better mixing of the substrate with the groundwater than introducing the substrate as a solution. Another advantage is the relatively low costs of injecting gas at great depths. Earlier tests indicated that due to the stirring created in the soil by the injected gas (input of energy), contaminants are more readily available for biological degradation or physical removal, which is a favorable side-effect of the method (Tonnaer et al., 2001).

Objective. The objective of this research was to demonstrate in a field pilot test that injection of a substrate with nitrogen carrier gas is a feasible alternative to the in-situ remediation methods commonly applied to remediate CAH. The following aspects of gas injection were investigated:

- radius of influence and distribution pattern of the injected gas;
- effects of the injected substrate on the degradation rate of PCE, the original contamination.

2. MATERIALS AND METHODS

A pilot scale injection system consisting of a single injection well was installed at a depth of 43 m below grade. Figure 1 gives a schematic representation of the pilot setup. A number of nested monitoring wells was installed at a distance of 2, 4 and 6 m from the injection well at depths of 14-15 m, 24-25 m, 34-35 m and 43-44 m below grade.

Figure 1: Schematic view of the pilot setup and spatial distribution of biodegradation

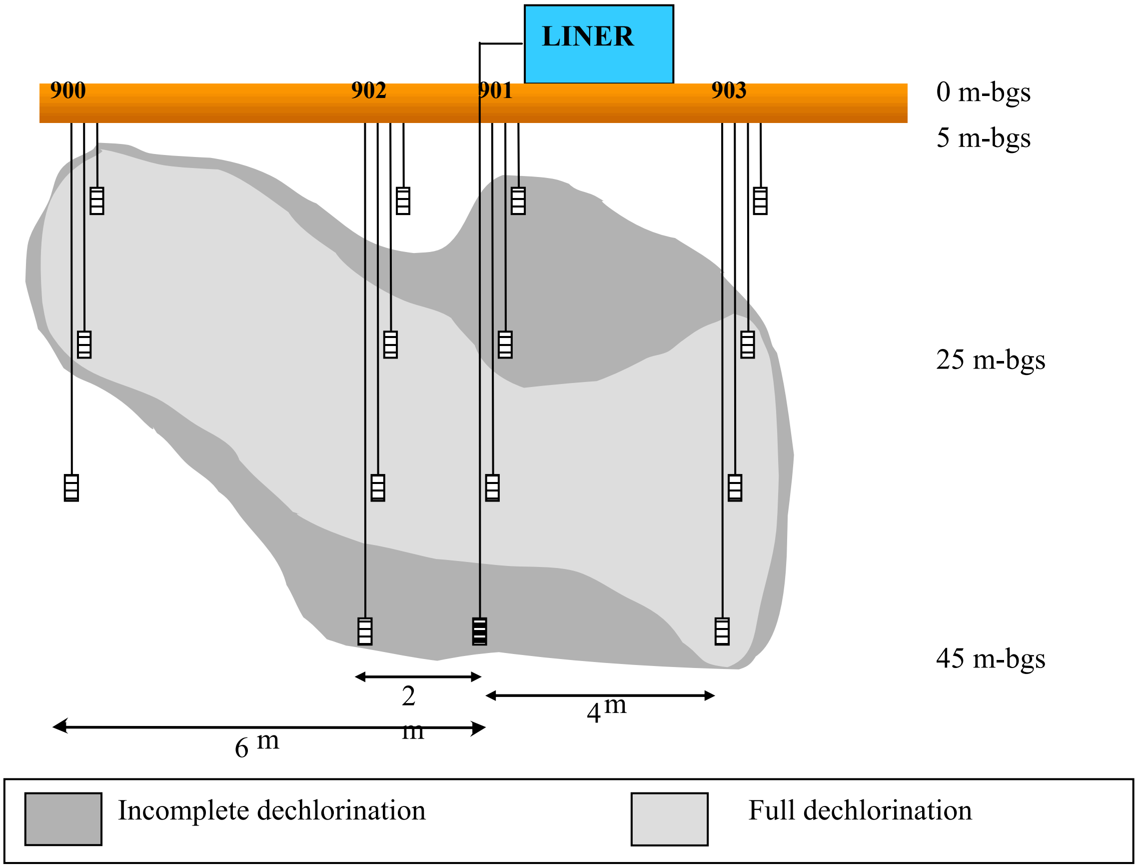


Figure 2: LINER pilot test setup

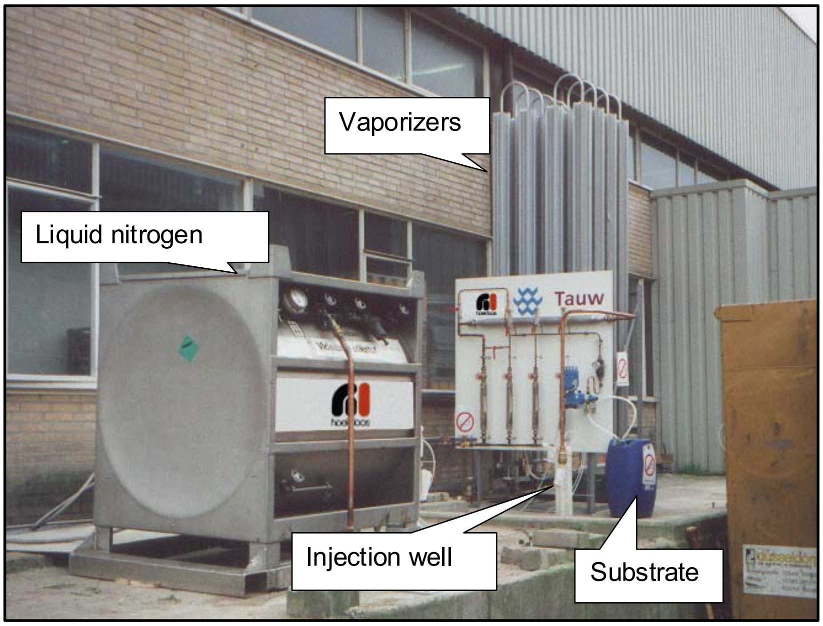


Figure 2 shows the LINER pilot test setup. Liquid nitrogen is vaporized and the gas pressure is reduced to the appropriate injection pressure. Methanol is nebulized into the nitrogen gas flow using nozzles.

Methanol was used because in several lab studies and field tests at other sites it proved to be a good substrate to enhance biodegradation of CAH. During the first 12 weeks of the pilot study, methanol was used as substrate. Nitrogen gas was injected daily for 4 minutes per day. About 10 m^3 of nitrogen gas and about 1 L methanol was added per injection.

After 12 weeks, the substrate was changed to a mixture of ethyl lactate and methanol (50/50 vol %). Each month monitoring wells were sampled and analyzed for CAH, ethene, and ethane. In addition, methanol, ethyl lactate and ethanol (ethyl lactate disintegrates into ethanol and lactate) were occasionally analyzed at a selection of the monitoring wells.

Before the first substrate injection and after about 30 weeks, sulfate and methane were measured to see whether substrate addition affected electron acceptor concentrations.

3. RESULTS AND DISCUSSION

Substrate distribution. At the injection location, methanol has been measured in high concentrations, ranging from 130 mg/L at a depth of 34 m bgs to 570 mg/L at a depth of 14 m bgs. This vertical distribution of methanol indicates the methanol vapor to be sufficiently stable to be distributed by the nitrogen gas flow. Also ethyl lactate and ethanol were detected after injection at the location of injection over this large range in depth.

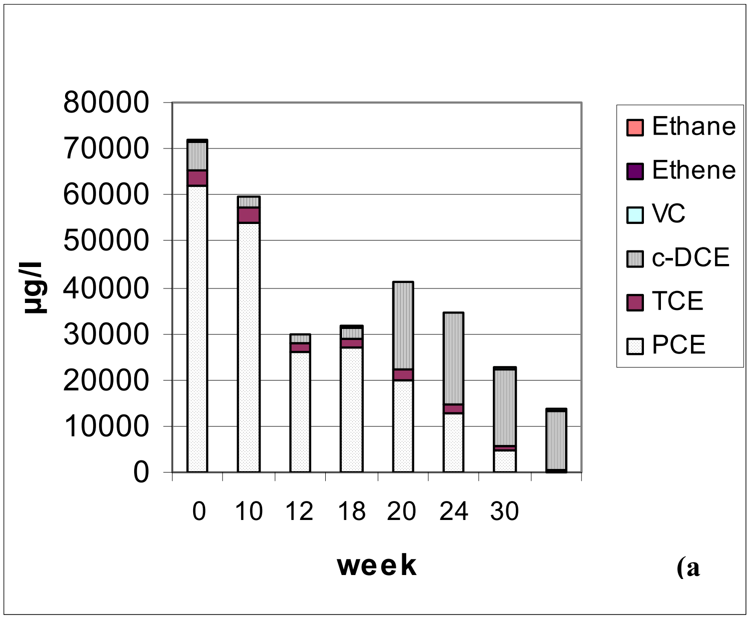
No methanol, ethyl lactate, or ethanol, however, were detected in monitoring wells located laterally from the injection well. Because of the high detection limit of methanol (2 mg/L), combined with biological consumption, methanol may have reached the wells without being detected. Based on substrate measurements, no clear distribution pattern of substrate could be observed.

Stimulated biodegradation of CAH. Since it became obvious that the distribution of substrate could not directly be assessed by substrate analyses, analyses of CAH and degradation products were intensified. In

Figure 1 the extent to which CAH degradation was stimulated is shown qualitatively. The light color represents the area where transformation of the CAH to the end product ethene was accomplished. The dark color represents the area where dechlorination was incomplete and stopped at *cis*-dichloroethylene.

In Figures 3 and 4, results of two monitoring wells are shown that are representative for complete degradation to ethane (Figure 4) and incomplete degradation to *cis*-dichloroethylene (Figure 3). During the first 12 weeks no shift in the relative concentrations of the CAH or their degradation products was observed in either well and therefore no significant biodegradation occurred. After 12 weeks, another substrate was used (mixture of methanol and ethyllactate) and biodegradation clearly started. The total concentration of degradation products increased compared to concentrations of PCE, the initial compound. It is not clear whether the enhanced biodegradation is a result of switching substrates, or whether the end of a lag in microbial growth was reached.

Figure 3: Absolute concentrations (a) and relative concentrations (b) of PCE and its degradation products as a function of time at the location of Injection Well 901 at 14 m bgs.



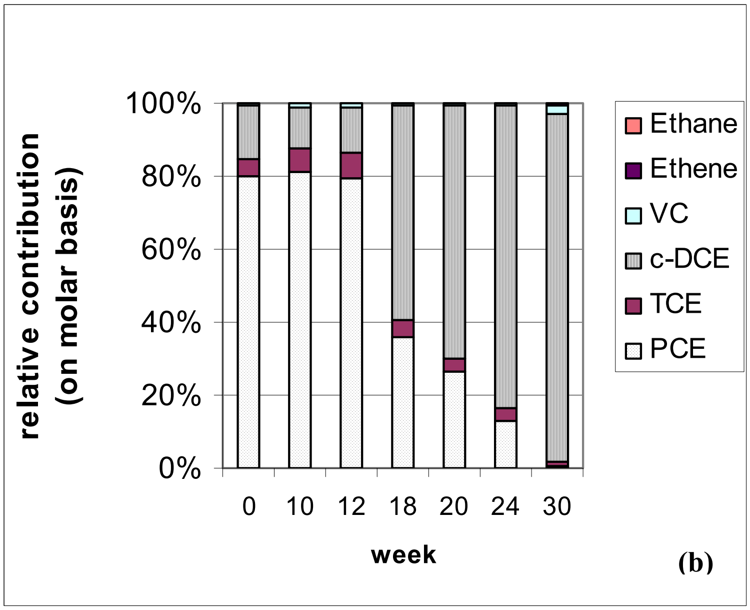
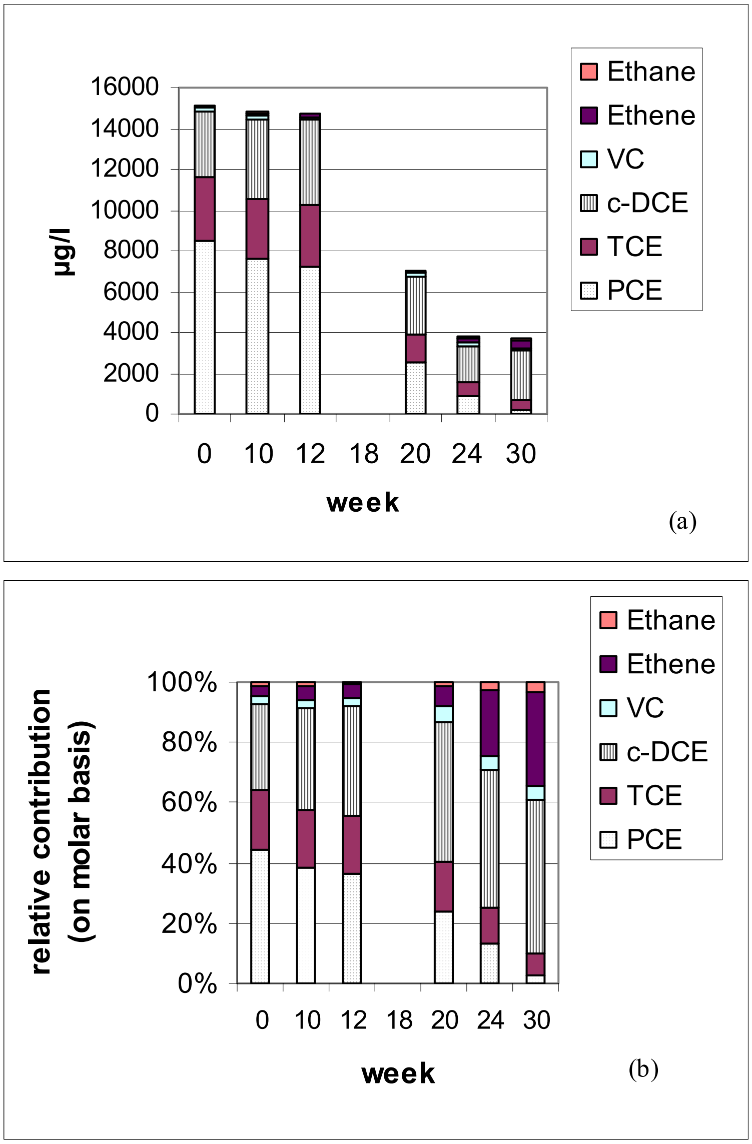


Figure 3a shows a significant decrease of the PCE concentrations in Monitoring Well 901 (14-15 m bgs). The TCE concentration remained about constant, indicating that TCE rapidly was converted to *cis*-dichloroethylene. The degradation seemed to stagnate at *cis*-dichloroethylene. A possible explanation is that there was not enough biomass yet to convert *cis*-dichloroethylene to vinyl chloride. Figure 3b shows the relative contribution of the different compounds to the total molar concentration of ethenes. The relative contribution of c-DCE increased significantly while PCE was almost been depleted.

Figure 4: Absolute concentrations (a) and relative concentrations (b) of PCE and its degradation products as a function of time at 4 m distance from Injection Well (monitoring well 903 at 43 m bgs).



In Monitoring Well 903 at 4 m distance from the injection well and 43 m bgs a significant decrease in PCE and TCE concentrations was observed (Figure 4a). PCE was almost depleted and a complete transformation to ethane occurred.

Electron acceptor processes. Before the start of the pilot test, sulfate concentrations ranged from 63 to 82 mg/L and did not change significantly during the test (30 weeks). Only in well 901 (at the location of injection) did sulfate concentrations decrease to about 20 mg/L. Methane concentrations were < 1 mg/L before the start of the test and concentrations did not increase. Methanogenesis apparently was not stimulated by the addition of the substrates. Because the addition of the substrates resulted in chloroethene transformation without significant sulfate reduction and methanogenesis, the lack of substrate, not unfavorable electron acceptor processes, must be the cause of the absence of biological degradation under natural circumstances.

Based on the results of the pilot test, LINER appears to be a promising technique for distribution of substrates in the subsurface. At the site of the pilot test a full-scale remediation will be carried out using LINER.

4. ACKNOWLEDGEMENTS

The Dutch Soil Research Program (SKB), Philips, the province of Gelderland and the Province of South Holland are acknowledged for their financial support.

5. REFERENCE

Tonnaer, H., E.C.L. Marnette, P.A. Alphenaar, C.H.J.E. Schuren, K.M.J. van den Brink. 2001. LINER-gasinjectie. Een nieuw concept voor de stimulering van de biologische CKW-afbraak. Report nr. SV-080, CUR/SKB, Gouda, The Netherlands (in Dutch).

Project No. 26

SIREN: Site for Innovative Research on Monitored Natural Attenuation

Location	**Project Status**	**Contaminants**	**Technology Type**
United Kingdom	Ongoing	Organic solvents	Monitored natural attenuation (MNA)
Technical Contact	**Project Dates**	**Media**	
Theresa Kearney, National Groundwater and Contaminated Land Centre Environment Agency Olton Court, 10 Warwick Rd, Olton, Solihull, West Midlands B92 7HX	September, 1999-~2003	Consolidated and non-consolidated aquifer	
	Costs Documented?	**Project Size**	**Results Available?**
	Yes	>£1 million	Yes

The information in this project summary is current as of January 2002.

1. INTRODUCTION

SIReN is the acronym for the Site for Innovative Research on Monitored Natural Attenuation (MNA). This project aims to promote the application and understanding of MNA in the UK. The overall aims of the project include 1) the identification of a site which could potentially allow the demonstration of natural attenuation under UK conditions, and 2) the use of that site for the development of research projects studying the fundamental aspects of natural attenuation processes. The SIReN site, once characterized, will be open to any bona fide researcher to conduct research on natural attenuation funded from other bodies. The project was developed by AEA Technology, Shell, the Environment Agency and CL:AIRE (Contaminated Land: Applications in Real Environments). In Phase 1 of the programme the project team selected a UK site suitable for research into MNA selection. The criteria used for site selection included: long term site availability (3-5 years); a suitably complex mixture of contaminants; an aquifer characteristic of UK conditions. In Phase 2 of the program a detailed site characterization was/is being performed. In addition, three different guidelines for MNA were benchmarked (the UK Environment Agency Guidelines (Environment Agency, 2000), the ASTM Standard Guidelines (ASTM, 1998) and the NICOLE –TNO draft MNA Protocol. Finally, Phase 3 of the project includes management of research at the site and dissemination of information gained through said research. Herein, we present the results of the site selection (Phase 1), up-to-date site characterization and the results of the benchmarking exercise (Phase 2) and the status of the ongoing research at the SIReN site (Phase 3).

2. BACKGROUND

Many organic contaminants degrade naturally in the biosphere without the interference of man. The biogeochemical processes that recycle organic and inorganic compounds occur naturally on many contaminated sites and can be harnessed to mitigate risks to human health and the environment associated with the contamination. Monitoring such transformations and modeling their long-term performance can be a useful alternative remedial tool. Termed “monitored natural attenuation”, this approach has been shown to be effective over a range of sites, especially when compared with more engineered solutions (Brady et al., 1997; Wickramanayake and Hinchee, 1998). Although MNA has been demonstrated at a range of sites (Thornton et al., 1999; Brady et al., 1997; Begley et al. 1996), there is still a dearth of research into MNA in minor sedimentary aquifers and in particular those situated on consolidated formations. Such conditions are not uncommon in the UK.

Assessment of natural attenuation requires knowledge of the in situ contaminant mobility, and the biological, chemical and physical decomposition processes of the contaminants. There is growing awareness of MNA amongst regulators, problem owners, property developers, future property owners, and consultants in the UK; however, a well-documented demonstration of MNA at a complex site will have an important role in improving further understanding of this approach. It is for this reason that the SIReN project has been established, with the results of the site selection (Phase 1), an initial site characterization and a MNA guideline benchmarking exercise (Phase 2) and the status of ongoing research projects (Phase 3) presented herein.

3. TECHNICAL CONCEPT

Natural attenuation is the process by which organic contaminants degrade in the biosphere by natural biogeochemical processes such as biodegradation, reduction, hydrolysis, sorption, dilution and dispersion (ASTM, 1998). Monitored natural attenuation is the term used to describe the process of monitoring and demonstrating such transformations, and modeling long term performance.

4. ANALYTICAL APPROACH

Presented below is the analytical approach taken in Phase 1 of project SIReN. To find a suitable demonstration site for monitoring natural attenuation, a number of sites were reviewed. Criteria were identified to assess the suitability of the sites for Project SIReN. The ideal site should:

1. Site available for 3-5 years
2. Biodegradable groundwater plumes
3. No ongoing remediation process
4. Good site data available.
5. Have contamination in a consolidated aquifer

A site chemical plant located in the North West of England was selected as the site for SIReN. During Phase 2 of SIReN, verification of the subsurface conditions and the potential for natural attenuation was needed before research could begin in earnest. The data from these analyses are included below. Also included in Phase 2 was the benchmarking exercise of 3 MNA guidelines. Finally, research has been ongoing at the site over the past 24 months and the research project titles and authors are detailed below.

5. RESULTS

Phase 1: Over 200 sites were considered. Of these a site was selected in the north west of England. This site was a single owner chemical plant with mixed contaminants including BTEX, chlorinated solvents, LNAPL, and DNAPL. The project team agreed that the contamination could be managed successfully by monitored natural attenuation (MNA).

Phase 2: Having chosen the demonstration site for SIReN, verification of the subsurface conditions and the potential for natural attenuation was needed before research trials could begin in earnest. Therefore, Phase 2 of SIReN involved a detailed site characterization using readily available data. To supplement the understanding of the groundwater regime mathematical modeling was also carried out. A report summarizing the conceptual understanding of the geology, hydrogeology, and contaminant fate and transport is now available (Environment Agency 2001a).

The site typifies many of the industrially contaminated sites in the UK, in that manufacturing has taken place for many years and it is close to major surface water courses. The main aquifer beneath the site is a sandstone that is overlain by thick, low permeability glacial clay deposits. This is also typical of northern industrial sites in the UK. Four distinct geological strata were identified (layers 1 to 4) during the site characterization. There are two (and possibly 3) water bearing units at the site and these are separated by a relatively impermeable layer or aquitard. The latter restricts the vertical migration of water and /or contaminants to the aquifer below. The groundwater is not used locally for drinking but is a significant source of water for irrigation and industrial use.

There are two contaminant source zones in the ground and evidence that some contamination has reached the groundwater. The contaminants are mainly hydrocarbons (predominantly benzene, ethylbenzene, toluene and xylene) with some naphthelene, styrene, and chlorinated aliphatic hydrocarbons). The current understanding of the contaminant distribution is derived from soil analysis and groundwater samples from boreholes. The results suggest that dissolved phase contaminants are migrating within the groundwater body in a north north-westerly direction. There is evidence that natural attenuation is occurring within the contaminated zone.

Mathematical modeling was used to predict the fate and transport of the contaminants in the groundwater. This shows that the contaminated groundwater plumes are unlikely to extend more than 250 m from the source and that they would continue to migrate for approximately 15 years after the contamination entered the ground and then stabilize. Eventually natural attenuation processes would cause shrinkage of the plumes. Despite having characterized the site successfully a number of questions remain unanswered about subsurface flow mechanisms and contaminant migration pathways. To address these a second phase of investigation was initiated. This was designed to improve the data set by employing field testing methods which include sampling and analysis of newly installed data points. This work is on-going and will be reported on in 2002.

The MNA guideline benchmarking exercise was also carried out during SIReN Phase 2, the details of which can be found in an Environment Agency report (Environment Agency, 2001b). Of the three Guidelines/protocols included in the study the Agency guidelines were shown to compare well with the ASTM and NICOLE-TNO protocols. In part due to the tiered system of lines of evidence, the ASTM guidelines proved easiest to apply and were the most transparent. However, the Agency guidelines also provided for transparent decision making, did not require application of a model if evidence of MNA was considered decisive, and was more defensible than the ASTM system. Moreover, because of the requirement for regular regulatory monitoring, the Agency guidelines had the least potential for accidental delay and could therefore prove to be more cost effective than the other systems. It should be noted however, that the potential for bottlenecks does exist when applying the Agency guidelines. In particular, the requirement for regular regulatory involvement in decision making may potentially result in resource implications for the regulatory bodies. To offset this, clear procedures should be established for the submission of MNA ‘case’ information with clear systems also set up to data review once utilization of MNA is agreed.

Phase 3: As a part of SIReN phase 3, 4 research projects have been ongoing. These are as follows:

- Predictive modelling of organic contaminant migration at a petrochemical site (Daniel Benitez Galvez, MSc Thesis Imperial College London).
- Application of the Environment Agency MNA guidelines to data from the site (Angela Sheffield MSc Thesis, Nottingham)
- Investigation into methods for speciating Iron in the Groundwater (supervised by Simon Bottrell (Leeds);
- Microbial Ecology: Factors Influencing Natural Attenuation in a Contaminated Sandstone Aquifer (Anne Tucker, PhD Thesis, Essex).
- Results from each of these will shortly be available on the SIReN website (www.claire.co.uk/siren/index.htm).

6. HEALTH AND SAFETY

The site investigation work was carried out using the best available techniques to minimize the potential impacts.

7. ENVIRONMENTAL IMPACTS

The project aims to confirm natural attenuation and therefore will provide evidence of improvements in the groundwater quality with time. This will represent a reduction in the environmental impacts.

8. COSTS

The overall costs of the project are as follows:
The total Environment Agency contribution is estimated to be ~£150,000, with £ 25,000 provided for Phase 1 and £124,729 in Phase 2. During phase 1, over £1 million worth of site investigation reports were reviewed. During Phase 2, in kind contributions from the project team should total ~£120,000. Through phase 3, the project team in kind contributions should be ~ £143,000 and are looking to manage ~£1 million per year in research grants.

9. CONCLUSIONS

Phase 1: During the first phase of the project over 200 sites were considered as possible field locations. From these sites, a single owner chemical plant was selected for the SIReN project.

Phase 2: The site owners have since granted permission for Phase 2 of project SIReN to go ahead, and have agreed for the site to be used as a demonstration site for 3-5 years subject to certain conditions of confidentiality and safety. Characterization of the SIReN site is underway and the current understanding is that there is/are:

1. 4 different geological layers;
2. 2 possibly 3 water bearing zones;
3. 1 aquitard;
4. groundwater flows towards surface waters (i.e. north and north-west); and
5. evidence of contamination in the soil and migration into groundwater.

Phase 2 (MNA benchmarking): The Agency guidelines compared well with both the ASTM and NICOLE-TNO protocols. These guidelines have since been applied to the SIReN data by Ms Angela Sheffield in her MSc thesis entitled ‘Application of the Environment Agency MNA guidelines to data from the SIReN site’. Results of this application will be presented in 2002.

Phase 3: Four research projects have been, or are being, carried out at the site. Further applications for research funding are in process. Preliminary groundwater modeling suggests that the contamination is unlikely to migrate beyond 250 m from the source zone and will stabilize in approximately 15 years. This site will therefore be available to the research community for at least the next 3-5 years.

10. REFERENCES

1. Environment Agency 2000 R&D publication 95: Guidance on the Assessment and Monitoring of Natural Attenuation of Contaminants in groundwater.

2. ASTM Standard Guide for remediation of Groundwater by Natural Attenuation at Petroleum release sites. American Society for Testing and Materials Annual Book of ASTM Standards, ASTM. Philadelphia, PA.

3. Brady P.V., Brady M. and Borns D.J. (1997) Natural Attenuation: CERCLA, RBCAs and the Future of Environmental Remediation. Lewis Publishers, USA

4. Wickramanayake G.B., and Hinchee R.E. (1998) Natural Attenuation of Chlorinated and Recalcitrant Compounds. Battelle Press, USA.

5. Thornton S.F., Lerner D.N., and Banwart, S.A. (1999) Natural Attenuation of phenolic compounds in a deep sandstone aquifer. In Proceedings of 1999 Bioremediation Conference. Volume 5: pp. 277-282., Battelle Press, USA.

6. Begley J., Croft B.C. and Swannell R.P.J. (1996) Current Research into the bioremediation of Contaminated Land. Land Contamination & Reclamation 4: 199-208.

7. Environment Agency 2001a Project SIREN: Phase 2a Conceptual Site Model & Groundwater Model Technical report P2-208/TR/2 ISBN 1 85705 6027.

Project No. 27

Hydro-biological Controls on Transport and Remediation of Organic Pollutants for Contaminated Land

Location Former gas works site, United Kingdom	**Project Status** New project	**Contaminants** PAHs, phenols, substituted benzenes	**Technology Type** In situ bioremediation
Technical Contact Prof. Howard Wheater Department of Civil & Environmental Engineering, Imperial College of Science, Technology & Medicine, London, SW7 2BU	**Project Dates** February 1998 – February 2001	**Media** Soil and groundwater	
	Costs Documented? Yes	**Project Size** Not available	**Results Available?** No

The information in this project summary is current as of January 2000.

1. INTRODUCTION

The research will (a) investigate contaminated soil at a representative former gasworks site and quantify the physical, hydrological and chemical characteristics and assess the transport of organic contaminants to groundwater; (b) In situ microbial biodegradative activity will be evaluated using reverse transcriptase polymerase chain reaction (RT-PCR) techniques and the potential for enhancement assessed and tested; (c) The information on biodegradative activity will be incorporated within a modeling framework, in order to predict the long-term impact of current and enhanced in situ bioremediation; and (d) The model will be developed as a decision support system to provide guidance for bioremediation design for groundwater protection.

The project objectives are to:

1. Investigate polynuclear aromatic hydrocarbon (PAH), phenol and aromatic hydrocarbon contaminated soil and groundwater at a representative former gas works site and quantify the physical, hydrological and chemical characteristics, including spatial and temporal variability.

2. Assess in situ biodegradative activity in the vadose/unsaturated zone and evaluate potential for enhanced bioremediation.

3. Incorporate the information on biodegradation activity within a modeling framework incorporating hydrological and geochemical controls on microbial activity and hence to predict long term impact of current and enhanced on-site biodegradation on groundwater.

4. Develop the model as a decision support tool for assessing the potential for remedial design to reduce the risk of groundwater pollution and thereby provide aquifer protection.

2. BACKGROUND

The research is focussed on a case study contaminated field site, belonging to BG Property Holdings Ltd. The research is laboratory and field-based and directed towards developing field-scale relationships and techniques over a period of three years. Extensive site characterisation is being undertaken to a research level to define the spatial heterogeneity of the hydrological, geochemical and microbial conditions.

3. TECHNICAL CONCEPT

The research programme focuses on the vadose zone and capillary fringe, and soil-groundwater interactions, with respect to behaviour of PAH contaminants typically found on gasworks sites (coal tar constituents). It seeks to evaluate transport of organic contaminants in the vadose zone in order to assess their impact on groundwater pollution. The programme looks at identifying in situ biodegradation processes that may be occurring in the subsurface. We seek to identify and quantify the natural processes and rates. A new methodology is being applied to define in situ microbiological activity (see below). Natural processes have been identified and the potential and limiting contaminant degradation rates of these processes will be estimated and implications for clean up quantified.

An important aspect of the microbiological analysis is that the actual and potential level of activity can be identified. The detailed analysis of site variability is indicating the likely factors limiting microbial activity, and the potential for enhanced microbial activity is being investigated through manipulation experiments in the laboratory and on site considering, for example, hydrological controls on redox status, enhanced oxygen and nutrient supply, and effects of toxicity. Bioventing is being applied in situ.

To represent the interdependence of hydrological, chemical and biological controls on microbiological degradation of contaminants, a numerical model of unsaturated zone flow and transport processes is being developed at Imperial College. This provides a vehicle for data assimilation and analysis. The model will be used to assess the effects on groundwater pollution through bioremediation. This will provide both a decision support system for remediation options and a tool for presenting assessment options to regulators.

4. ANALYTICAL APPROACH

To define the hydrological fluxes, in situ soil and groundwater conditions, and soil and groundwater hydraulic properties, conventional borehole cone penetrometry techniques, piezometer and geophysical techniques are being used (including EM39 borehole logging and electrical resistance tomography) in conjunction with pumping tests. This is supplemented by specialist soil monitoring equipment (tensiometers, neutron probe, in situ permeametry, air permeametry and O2/CO2 respirometry probes).

The spatial location and chemistry of contamination will be investigated in detail using conventional methods of core analysis from boreholes and trial pits, with detailed analysis of soil water, groundwater, non-aqueous phase contaminants and soil and aquifer geochemistry.

A major focus of the programme is to determine the intrinsic bioremediation. The majority of bioactivity assessment methods employed to date have been based on the measurement of microbial metabolism (e.g., dehydrogenase activity or adenylate concentration), which is not related to specific catabolic functions, or 14C-mineralisation assays, which are conducted ex-situ and represent catabolic potential rather than in situ activity. Recently, methods have been developed at King’s College for monitoring specific in situ catabolic gene expression using direct isolation of mRNA from contaminated soils. King’s College has also successfully developed the reserve transcriptase-polymerase chain reaction (RT-PCR) technique for the quantification of specific mRNAs from environmental samples. Hence a novel bioassay system will be applied to cores from the site.

Following initial site characterisation, appropriate locations and substrates will be defined for a series on on-site manipulation experiments to investigate the potential for enhanced degradation. Previous work by Smith and Bell (Pieltain 1995) has demonstrated complex effects of PAH mobility in the hydrological environment which can affect redox status and bioavailability. Depending on site conditions, hydrological and chemical controls will be investigated in addition to manipulation of oxygen and nutrient status. Possible field trials will include addition of moisture and nutrients via an infiltration system, oxygenation by passive venting (bioventing), or oxygen release compound systems, or more active means such as air-sparging, or by addition of hydrogen peroxide. Effects of toxicity of co-contaminants will be considered.

5. RESULTS

The effects of biodegradation will be incorporated in a modeling framework. An underlying deterministic model will be developed, based on the SPW and SLT codes developed at Imperial College (Karavokyris, Butler and Wheater, 1990, Butler and Wheater, 1990), which represent soil-plant water interactions. A biochemical model component will be introduced to simulated effects of microbial degradation in response to nutrient, moisture and oxygen availability, and coupled with soil water and gas flow models to provide time-dependent degradation rates, and transport of soluble waste products. A framework for the analysis of uncertainty in soil contaminant transport models has recently been developed at Imperial College in collaboration with Prof.G.Dagan (Tel Aviv). This will be extended to include effects of heterogeneity in microbial processes through 1-D stochastic simulations. The model will be applied to the interpretation and generalisation of the site-specific data. The effects of quantified biodegradation rates on in situ biodegradation will be examined in the context of climatological, hydrological and geochemical controls and evaluated in comparison with site data. The results of the detailed modeling will be incorporated in a simpler, rule-based procedure to provide a management tool to evaluate site management options, and to produce long-term response within a framework of risk management.

6. HEALTH AND SAFETY

A health and safety programme has been developed for the fieldwork component of the project.

7. ENVIRONMENTAL IMPACTS

No significant environmental impacts of the project have been identified.

8. COSTS

The cost of the project is estimated to be $605,000 over three years.

9. CONCLUSIONS

The anticipated outcomes of the project are as follows:

- Assist in the development of an effective on site remedial treatment of typical gas works contaminants.
- Develop a better understanding of the underlying processes of bioremediation at field scale and the effects of the physical and chemical heterogeneity associated with disused industrial sites and made ground.
- Design tools to translate the knowledge learnt into practical techniques for site characterisation and application.

10. REFERENCES

1. Butler, A.P. and Wheater (1990) Model sensitivity studies of radionuclide uptake in cropped lysimeters. Nirex Safety Series report NSS/R253, UK Nirex Ltd.

2. Karavokyris, I., Butler, A.P., and Wheater, H.S. (1990) The development and validation of a coupled soil-plant-water model (SPWI). Nirex Safety Series report NSS/R225, UK Nirex Ltd.

3. Pieltain, F.J.M. (1995) The effect of different rainfall regimes and drainage conditions on the mobility of PAHs from soil contaminated with coal tar. Ph.D. thesis, University of London.

Project No. 28

Demonstration of a Jet Washing System for Remediation of Contaminated Land

Location	**Project Status**	**Contaminants**	**Technology Type**
Former refinery site, Southern England	New Project	Tars, petroleum hydrocarbons.	Ex situ soil washing
Technical Contact	**Project Dates**	**Media**	
Tony Wakefield Wakefield House Little Casterton Rd Stamford Lincolnshire PE9 1BE	August 2000 – September 2000	Soil and made ground	
	Costs Documented?	**Project Size**	**Results Available?**
	Yes	Demonstration	No

Project 28 was completed in 2000.

1. INTRODUCTION

This project will demonstrate the application of an ex situ process-technology to the remediation of soil and other solid wastes that are contaminated with organic residues at a former refinery site. The demonstration will take place over a six-week period in August-September 2000 during which time over 500 tonnes of material will be processed. In addition to the refinery wastes, the project will also include the processing of materials from gasworks reclamation and materials from other oil industry sources.

The project is supported by exSite, a registered environmental body that uses funding from the UK landfill tax scheme to facilitate a research programme focusing on brownfield land regeneration. The work is being carried out Eurotec Land Remediation Ltd.

2. BACKGROUND

This project aims to demonstrate the successful transfer of technology from the mining industry to the remediation of land affected by contamination. Jet pump technology has been used by the mining industry for a number of years as a means of high capacity materials handling over long distances. It is particularly suitable for dealing with sand, gravel and soil, using water as the carrying medium. The heart of the process is a self-priming pump with no moving parts. It can handle 120 tonnes of material per hour with minimal operational maintenance. A feature of the jet pump, in its original application, is its relative inefficiency in imparting ordered energy to the material that is pumped. This characteristic has been exploited in the development of the jet pump scrubber that will be demonstrated by this project.

3. TECHNICAL CONCEPT

The heart of the scrubber is a jet pump. A jet pump accepts fluid energy rather than energy supplied via a rotating shaft. It has no moving parts. It operates by a process of transfer of energy by shearing forces, a turbulent process in which spinning cells of fluid interact between the incoming and the motive fluids. The process is inefficient at pumping because the greater part of the energy input is lost to turbulent dissipation. However, the reverse is true for a scrubber because of the cleaning action of the turbulence.

In addition to the turbulence the scrubber also cleans particles by:

Direct contact between solid particles. Where particles are small in comparison with the diameter of a turbulence cell they are forcibly rubbed together.

Cavitation. By raising the driving pressure in the pump, the turbulence cells spin so fast that the associated centrifugal force causes such a vacuum at the centre of the cell that the water boils. As these

"Bubbles" collapse. A violent dissipation of energy occurs, helping to breakdown the binding between contaminant and solid particle.

In operating the scrubber it is possible to create an intensity of energy dissipation of up to 20MW/m3. The pressure and temperature of the scrubber can be carefully controlled to optimise performance. The scrubber uses water as its carrier medium.

The scrubber has been used to separate surface contaminants from solid particles including the removal of adherent clays and iron oxide from quarry product and the removal of crude oil from contaminated beach sands. This demonstration will evaluate its effectiveness for separating contaminated tar and oils from excavated soil and made ground.

4. ANALYTICAL APPROACH

No details are currently available.

5. RESULTS

No details are currently available.

6. HEALTH AND SAFETY

No details are currently available.

7. ENVIRONMENTAL IMPACTS

No significant environmental impacts of the project have been identified.

8. COSTS

The cost of the project is estimated to be £100,000 for the trial.

9. CONCLUSIONS

No details are currently available.

10. REFERENCES

None.

Project No. 29

Automatic Data Acquisition and Monitoring System for Management of Polluted Sites

Location	**Project Status**	**Contaminants**	**Technology Type**
Italy	In progress	TPH, BTEX	Remote monitoring
Technical Contact Dr. Gilberto Latini Dr. Claudio Mariotti Dr. Armando Sechi Dr. Leonardo ZAN AQUATER S.p.A. Via Miralbello 53 61047 S.Lorenzo in Campo (PS) Italy Tel: (+39) 0721 7311 E-mail: leonardo.zan@aquater.eni.it armando.sechi@aquater.eni.it	**Project Dates** Start: January 1998 End: February 2001	**Media** Groundwater, soil, air	
	Costs Documented? Not yet available	**Project Size** Prototype	**Results Available?** Yes

The information in this project summary is current as of January 2002.

1. INTRODUCTION

This project deals with an automatic remote and on-site environmental monitoring system designed and implemented to control remediation processes in sites contaminated by petroleum and its by-products (other compounds can also be monitored). The monitoring system is PC based (such as a remote station), and doesn't require any further PC running on site to control the remediation process and data acquisition, but only sensors to acquire data on the parameter/process to be monitored. An AD converter with internal processor coupled with modems (analogue, radio or GSM) monitors and automatically transmits data to any number of remote stations, as required by the user.

The system is based on National Instruments hardware running LabView software.
Process and monitoring data are stored on site and sent to the remote station on demand or at any desired frequency.

On-site alarms (out-of-range values, failures etc.) are automatically activated by the system and the alarm log can be received in the form of a SMS.

SMS can also be sent to the on-site station to activate any further instructions.

Data and process parameters can be automatically transmitted to an IP and published on a Web site, which can be accessed only by providing the user's name and password.

This project represents the state-of-the-art of a remote monitoring system.

2. BACKGROUND

The project started as a preliminary monitoring network developed under RESCOPP (Remediation of Soil Contaminated by Petroleum Products – P# EU-813), as a cooperation between Italian and French companies under the EU EUREKA Funding program during the years 1993-1997. Since then the project has been financed by the Research Funding Program of ENI (Italian Oil Company)

The project focused on developing innovative tools for monitoring remediation processes on sites polluted by petroleum products.

3. TECHNICAL CONCEPT

Control Process Parameters:

To monitor a remediation process it is essential to have knowledge on environmental media (components) and their interactions with water and pollutants. This means that the process is first developed on a theoretical basis, and then the monitoring system is implemented according to the results achieved.

Monitoring sensors are then placed where the process develops. Data bases linked to the system provide logs of events and the history of the monitoring activity. The minimum set of parameters to be verified in petroleum-polluted sites consists of:

Interstitial Gas

VOCs
CO_2
O_2
CH_4
Pressure

Soil in the Vadose Zone

Temperature
Humidity

Groundwater

Water level
Temperature
pH
Eh
Elec. Conductivity
Dissolved O_2
TPH
BTEX
Total heterotrophs

It might also be necessary to monitor the meteorological parameters that affect data evolution during all the processes involved in remediation.
These parameters are:

Temperature
Barometric pressure
Humidity
Solar radiation
Wind speed and direction
Rainfall

4. ANALYTICAL APPROACH

Measuring principles

The sensors connected to the monitoring system must assure that all data are measured with the same accuracy and validity as those measured in the laboratory.

System architecture

The system is composed of:

1. Sensors
2. AD converters with inner processor units
3. Software
4. HW (PC Pentium based)
5. Data transmission network (analogue, GSM or radio modem)
6. Monitoring wells
7. Measuring gauges
8. Analytical equipment for gas and water sampling

5. RESULTS

The system was installed in the Porto Marghera contaminated site (Venice, Italy) to test its effectiveness in monitoring and automatically managing a biopile process.
As the system is still a prototype, it only collects data referring to:

1. Hydrocarbons
2. Temperature
3. Humidity
4. Dissolved oxygen

The system is on-line since February 2001 and all collected data can be seen on Aquater's Website (www.aquater.eni.it/).

Another groundwater monitoring test has been carried out at Aquater's headquarters.
It consists in a groundwater source (monitoring well) activated by a local unit. The parameters of the pumped water (T, pH, DO, EC, and Eh) are measured by sensors. If the local unit reads an out-of-range parameter it activates a water sampler which collects and stores a sample or set of samples. The system also transmits a warning message (SMS) reporting the out-of-range parameter to the designated operator.

This monitoring system prototype meets the expectations required at this date.

6. HEALTH AND SAFETY

The system is totally safe as it avoids any handling of polluted water or soil.

7. ENVIRONMENTAL IMPACT

The aim of the project is to reduce the number of laboratory analyses and water–soil samples to a minimum, while increasing the capacity to monitor any type of remediation process from virtually anywhere in the world (no matter where the local station is located).

8. COSTS

The total cost of the project can be forecasted in 1 Million Euro (approximately 1.2 Million US $), 50% of which is required for the purchase of special sensors.

9. CONCLUSIONS

Based on the amount of data collectable by this system and thanks to the drastic reduction of laboratory analyses and site visits, it can be concluded that the system is very inexpensive and extremely cost-effective.

The alarm system prevents any loss of data for the final user.

The system is ready for use and enables continuous monitoring on any contaminated site. The monitoring activity can also be considered a long-term validation test following site remediation.

10. REFERENCE

RESCOPP project report (EUREKA Eu-813)

Project No. 30

Approved Biological Treatment Technologies for the Sustainable Cleanup of TNT-Contaminated Soil

<table>
<tr><td>Location
Clausthal-Zellerfeld, Germany</td><td>Project Status
Interim</td><td>Contaminants
TNT</td><td>Technology Type
Three different soil bioremediation technologies</td></tr>
<tr><td rowspan="2">Technical Contact
Dr. Jochen Michels
DECHEMA e.V.
Theodor-Heuss-Allee 25
60486 Frankfurt/Main
Germany</td><td>Project Dates</td><td colspan="2">Media
Soil</td></tr>
<tr><td>Costs Documented?
Yes</td><td>Project Size
Field-scale</td><td>Results Available?
Soon</td></tr>
</table>

The information in this project summary is current as of January 2002.

1. INTRODUCTION

The aim of the Joint Project "True to Scale Test of Biological Processes at the Former Ammunition Site 'Werk Tanne' with Assessment" is the evaluation and comparison of three on-site bioremediation procedures for TNT contaminated soil under field conditions with regard to efficiency, ecology and economy. The decontaminated soil material has been characterized by innovative analytical strategies to assess the ability of repositioning decontaminated soil heaps. The Joint Project is part of the Joint Research Group "Processes for the Bioremediation of Soil". This interdisciplinary group is developing innovative processes for soil bioremediation. It is logically divided into three columns of research: process development, backup research, and true to scale testing. The findings will be incorporated in the Handbook "Processes for the Bioremediation of Soil", which will be released in Oct. 2001. It is intended to assist the authorities and problem owners to find and select promising clean-up processes, thus contributing to the reusability of economically attractive sites.

2. BACKGROUND

The former ammunition site "Werk Tanne" near the city Clausthal-Zellerfeld in the Harz Mountains was one of the twenty former TNT production sites in Germany. With a monthly production capacity of 2,850 t TNT it was the fifth largest explosives production site of the third Reich. The site was built into a forested area of 119 ha and had two TNT production lanes. In contrast to other sites in Germany like "Stadtallendorf", "Hirschhagen" or "Krümmel", after World War II the area was not converted to an industrial site or a residential quarter. From 1992 the abandoned site was used for different approaches in the biological remediation of TNT-contaminated soil. From 1998 the Joint Project "True to Scale Test of Biological Processes at the former ammunition site 'Werk Tanne' with Assessment" has successfully tested three different biological remediation technologies in field scale.

3. TECHNICAL CONCEPT

A test area was prepared on the site for the three different remediation installations, including two tents and one building, safety areas regarding to safety of labor and safety of emission. The Industrieanlagen-Betriebsgesellschaft (IABG) takes over the central project management for the tasks of the site coordination, the scientific attendance and the planning for the required construction works. The site coordination ensures comparable conditions with regard to the treatments and the success evaluation. These conditions are (i) comparable soils and contamination; (ii) comparable analysis and documentation; (iii) comparable control soils and site conditions.

At different areas on the site "Werk Tanne" soil are taken and sieved to 60 mm. The soil was mixed frequently to ensure a homogeneous TNT contamination of 1,000 to 1,200 mg/kg soil (dm) throughout the pile before it was given to the soil treatment companies. The involved companies and procedures are:

Anaerobic/Aerobic Composting Process

The process by Umweltschutz Nord was originally developed by Bioremediation Inc. For the anaerobic/aerobic composting process the contaminated soil material was mixed with easy utilizable substrates to maintain anaerobic conditions and deposited into a pile. During the treatment term of about 12 weeks the soil pile was moved every 1 to 2 days in the beginning and only once a week afterwards. While the substrate was depleted during the treatment the pile shifted continuously from anaerobic to aerobic conditions. Transformation of the pollutants and immobilization of the transformation products occurred simultaneously during the entire process term. During two years four different batches of about 80 metric tons were treated. The initial concentrations of approx. 1,000 mg nitroaromatics per kg soil were rapidly reduced within 7 days. The concentration was durable below the detection limit of 0.5 mg/kg within three weeks. The maturing process to degrade the organic aggregates was concluded after 12 weeks. In cooperation with the involved authorities the decontaminated soil could be released on site.

Dynamic Pile Process

The dynamic pile process by Plambeck ContraCon is an anaerobic/aerobic treatment process with two distinct stages. The process was developed by the University of Marburg, Germany. During the anaerobic stage, which was maintained by easy utilizable substrates, TNT was transformed to reduced metabolites. The pile was static during the anaerobic stage, but after the switch to aerobic conditions the heap was aerated and the soil material was treated mechanically for the remaining term of about 12 weeks. The point of time to switch the conditions is dependent on the reduction stage of the nitroaromatics and occurs usually after half of the task. During the aerobic phase the reduction products were irreversibly bound to the soil organic matrix. During two years four different batches of about 32 metric tons were treated. The nitroaromatics were rapidly reduced to the corresponding amino(nitro-)aromic compounds during the anaerobic stage. After maintaining aerobic conditions the concentration of amino(nitro-)aromic compounds felt into the range of the detection limit. The refilling of the material on site was also permitted by the authorities.

White Rot Fungi Process

White rot fungi were cultivated in large amounts on straw and then were piled up in alternating layers with the contaminated soil material. During the static and aerobic soil treatment process by AWIA Umwelt the fungi proliferated through the soil matter and destructed the nitroaromatics with the aid of its extracellular enzyme system. Four different white rot and litter decaying fungi have been tested with 30 metric tons of contaminated soil material each. The process term was about a year; after 12 weeks the soil was mixed once and the straw/fungi substrate was renewed. A watering and aeration system was installed for maintenance humidity, nutrient supplementation, and aeration of the soil material in order to help the fungi to predominate over the soil-specific microflora for optimal detoxification. The aeration of the soil was carried out by an exhauster, which removed surplus water as well. Exhausted air and effluent were decontaminated afterwards. Especially in the final phase of decontamination, the concentration of harmful substances in the soil was minimized by addition of fresh cultures of the fungus. The TNT initial concentration of about 2.000 mg/kg (dm) could be reduced to 50 mg/kg soil material (dm). The refilling of the material on site was also permitted by the authorities.

4. ANALYTICAL APPROACH

A special scientific concept has been developed by IABG in cooperation with the authorities for the evaluation of the soil material and the processes. This includes the following test systems:

- Chemical analysis of nitroaromatics and known metabolites (incl. new described polar metabolites)
- Genotoxicological analysis (Ames-test)
- Ecotoxicological analysis (aquatic: Luminescent Bacteria (DIN); terrestric: Potential Nitrification (Swedish EPA), soil respiration (Swedish EPA), acute growth of higher plants (ISO), acute earth worm test (ISO))
- Physico-chemical soil characterization (pH, Corg, Nutrients, Soil Constituents)
- Human toxicological analysis
- Air monitoring

The backup research of the Joint Research Group had developed extended test systems for the ecotoxicological potential of the processed soil material using test batteries, humification process by NMR-spectroscopy with [15N]TNT, and long-term stability using [14C]TNT under simulated climatic worst case conditions.

5. RESULTS

The soil material could successfully been decontaminated by all three remediation processes and the material could be refilled on site. This was the first time that biologically decontaminated TNT-soil could be repositioned in Germany. The ecotoxicological tests showed no ecotoxicological hazard potential left in the soil material and the finished tests to the long-term behavior could show no remobilization of toxic metabolites. The results from the NMR-spectroscopy showed that TNT-metabolites are bound covalent to the soil organic matter and that they were further destructed due to the humification process.

6. HEALTH AND SAFETY

Different test systems were conducted according to the safety rules of labor:

- Biological material
- Air-monitoring (mononitrotoluenes, Germ pollution)
- Human toxicological test (TNT metabolites in urine, hemoglobine adducts)

7. ENVIRONMENTAL IMPACTS

Not available yet

8. COSTS

The individual process costs were calculated and appeared to be comparable to standard biological treatment costs of TPH-contaminated soil in Germany.

9. CONCLUSIONS

Biological remediation of TNT-contaminated soil is now an approved process in the meaning of sustainability. TNT metabolites will be humificated in the soil and destructed further in a way that no hidden hazardous potential will be left in the soil material.

10. REFERENCE

Michels, J, Track, T, Gehrke, U., and Sell, D. (Fachredaktion), Umweltbundesamt (Herausgeber). 2001. Biologische Verfahren zur Bodensanierung. Grün-weiße Reihe des BMBF (only available in German language).

Project No. 31

Phytoremediation Evaluation of Petroleum Hydrocarbon in Surface Soil

Location	**Project Status**	**Contaminants**	**Technology Type**
13 sites in US and Canada	Ongoing	Petroleum, PAHs	Plant enhanced bioremediation
Technical Contact	**Project Dates**	**Media**	
Steve Rock National Risk Management Research Laboratory 26 W. Martin Luther King Dr Cincinnati, OH 45268 Tel: 513-569-7149 Fax: 513-569-7879 E-mail: rock.steven@epa.gov	Accepted 2000 2001	Soil	
	Costs Documented?	**Project Size**	**Results Available?**
	Installation and start-up costs recorded	3- to 4-year field-scale test plots	Yes, preliminary

The information in this project summary is current as of January 2002.

1. INTRODUCTION

The Remediation Technologies Development Forum (RTDF) cooperative trials are designed to test the ability of plants to enhance degradation of petroleum hydrocarbons in surface soils. There are now thirteen field trial locations with two new sites in Canada. Results in progress are now available for six locations. As would be expected there is variation among the locations in the responses developing among the vegetation treatments. Two locations have statistically significant responses that indicate enhanced degradation in vegetated plots. One location is showing a promising trend. Treatment mean differences are not apparent yet in two locations. The ability to detect treatment differences appears to be related to the degree of prior weathering of the contaminants, the spatial variability of the contaminant at the sites, and perhaps the time needed for treatment effects to become apparent. It appears for less weathered contaminants, phytoremediation effects will become apparent within a couple growing seasons. It remains to be determined how plants will affect remediation on highly weathered sites.

Several lines of evidence, including microbial data may be helpful for indicating the presence of degrading organisms. The role of phytoremediation may ultimately be determined by a combination of the degree of weathering, the time available for treatment, and the determination of acceptable endpoints for remediation based on risk assessments and future site uses.

2. BACKGROUND

The TPH Subgroup of the RTDF, Phytoremediation Action Team initiated these trials to test the use of vegetation to enhance treatment of surface soils contaminated with weathered petroleum hydrocarbons. Collaborators include PERF (Petroleum Environmental Research Forum), USEPA, Environment Canada, the U.S. Department of Defense, major petroleum and energy corporations, environmental consultants, and university participants. The TPH Subgroup began meeting in March 1998 to develop a standard protocol for conducting cooperative field trials. Features of the protocol specify common procedures for each trial covering vegetation treatments, experimental design, analytical parameters, analytical laboratories, and data analysis. The RTDF protocol, initial site descriptions, and annual reports are available at http://www.rtdf.org.

3. TECHNICAL CONCEPT

The purpose of the project is to determine efficacy of agricultural and non-crop plants for degradation of aged petroleum hydrocarbons in soil at multiple locations and under varied climatic conditions. The standard plot size is 20' x 20' minimum, although the shape of the plots varies widely. There are four replications of each treatment. The statistical design is a randomized complete block (place plots based on presence of TPHs in site characterization. For soil and plant samples, take 8 random sample cores per plot and make a composite sample. The three standard treatments are as follows:

- Local optimized treatment: grass, mix of species, including trees
- Unplanted and unfertilized control (kept weed-free by post-emergent herbicide, hand-picking of weeds, or tilling).
- Standard Mixture of rye 10-15% (annual or perennial), legume 20-25% (alfalfa, clover, birds-foot trefoil), and fescue 60-70% (varieties chosen for local conditions).

Over the course of the trial, vegetated plots should be fertilized with nitrogen and phosphorus at the rate corresponding to the carbon to nitrogen to phosphorus ratio of 50:2:1. Additional fertilizer can be added to account for plant uptake requirements. All vegetated plots should be fertilized at the same rates. The rate of fertilization should be divided into several applications to minimize adverse effects on plant growth due to excess nitrogen. Accurate records should be maintained on rates of fertilization and how it is applied. After considerable discussion it was decided that the unvegetated treatment should not be fertilized so that the vegetation treatments are compared with a control that represents no treatment. This trial will not attempt to separate the effects of plants from the effect of fertilizer. Participants are encouraged to include an unvegetated and fertilized control treatment if space and resources permit.

Soil sampling: Eight random sub-samples per plot composited make one sample. Cores will be taken at 0 to 6” and 6” to 12". Take soil samples as described at the following times and soil depths sampling location at the following times:

T=I: Initial site characterization (after tilling) samples taken in grid over whole site.
T=0: Before planting, after seedbed preparation.
T=1: 6 months after planting, or end of first growing season.
T=2: 18 months after planting, or end of second growing season.
T=3: 30 months after planting, or end of third growing season.

4. ANALYTICAL APPROACH

- Agronomic conditions: pH, salinity, available nutrients, and soil analysis (texture, organic matter, EC, CEC, soil type). The analyses should be tailored to the region.
- Contaminant concentrations: PAHs using EPA method with GC, TPH using DCM solvent, TPH fractions using TPHCWG method.
- Microbial analysis (times 0 and 3 for plate counting and MPN, times 0, 1, 2, and 3 for PLFA and DGGE analysis).

5. RESULTS

Site A in California is located at an oil refinery. Data is available from samples taken at planting and the end of the first and second growing seasons. The analysis of variance and inspection of treatment means for Site A show no clear differences or trends among the treatments at either of the sampled soil depths. Large differences among the four replications and high variability in the data may be obscuring most treatment effects at this stage in the trial. The hydrocarbons at Site A are highly weathered. Our hypothesis concerning this site is that given the weathered nature of the hydrocarbons in the surface soils, it is going to be difficult to detect clear evidence of biodegradation.

Site B in Ohio is located on a former landfarm. The depth of soil sampling was changed between the initial Time 0 sampling and what has been called a second Time 0b sampling. Based on a new starting reference time, results are available after one growing season. The surface soil samples showed a general decline in concentrations from T0b to T1 although treatment means were not significantly different. There is an indication that all of the vegetated treatments declined in concentration more than the unvegetated control plots. This may indicate that treatment effects are developing.

Site F in New York is a former manufactured gas plant site. Analytical results are available from samples taken at planting and the end of the first and second growing seasons. The surface soil at Site F showed consistent declines in concentration of TPH and PAHs from Time 0 to Time 1 and from Time 1 to Time 2. By Time 2, there were statistically significant differences between the control plots and the willow/poplar plot for TPH and PAHs. All vegetated treatments had lower concentrations than the control plots for TPH and PAHs. There are a number of positive trends at Site F that may show an advantage of vegetation treatments given enough time. The less weathered surface soil may have more potential for further degradation than the deeper soil.

Site G in Kansas is utilizing sediments excavated from a motor pool waste lagoon. Analytical data is available from sampling at planting and at the end of the first growing season. After one year similar patterns were observed at the two soil depths. TPH concentrations began the trial in the range of 11000 to 16000 mg/kg and decreased to 5000 to 7000 mg/kg after one year. Concentrations of TPH and PAHs in the unvegetated control treatment decreased less than the vegetated treatments. Biomarker normalized data showed better statistical separation of the treatment means than the original TPH concentrations. Compared to the other RTDF sites, Site G showed the clearest response to the vegetation treatment after one growing season.

Site J in Arkansas is located at an oil production site. Only characterization data from the time of planting was available. Most of the contamination at this site is in the top 15 cm. PAH concentrations were lower at this site than the other RTDF sites. TPH concentrations were in the range of 10000 to 13500 mg/kg in the surface soil. The apparent low degree of weathering at this site may indicate a high potential for biodegradation.

Site K in Indiana is located at a former manufactured gas plant site. The contaminants are coal tar residues that extend from the soil surface to greater than 180 cm below ground. Hybrid poplars were planted as the single vegetation treatment. Soil was sampled to greater depths than the other field sites. Analytical results for priority pollutant PAHs are available from the time of planting and the end of the first two growing seasons. Based on the data received, there is no clear trend showing that PAHs are degrading in the vegetated treatments after two years.

Observable evidence of degradation is probably obscured by high variability among the plots with PAH concentrations ranging over an order of magnitude. Based on the data normalized to a high molecular weight PAH, there may be an indication that PAH levels are decreasing. Although trees have grown well at the site, a longer period of time may be needed to establish an effect of vegetation treatments at this location since treatment is desired in deeper soil than at the other field sites.

6. HEALTH AND SAFETY

No information available.

7. ENVIRONMENTAL IMPACTS

No information available.

8. COSTS

Phytoremediation-specific unit costs have been summarized for the first year at each of the field sites. The total startup costs ranged from \$16,854 to \$62,174 for the six sites. The operation and maintenance costs for the first year of the study ranged from \$16,500 to \$30,400. The total project costs for the first year ranged from \$38,392 to \$86,278. The calculated unit costs for the first year of the study ranged from \$4.00 to\$10.37/ft3.

9. CONCLUSIONS

Considered as a group, it appears some field sites will show significantly enhanced hydrocarbon degradation with vegetation treatments while other field sites may not show enhanced treatment during the time of the trials. Differences between field sites may be related to differences in hydrocarbon composition and weathering.

Project No. 32

Remediation of Chlorinated Solvents in Groundwater by Chemical Reduction Using Zero-Valent Iron, Pneumatic Fracturing, and Reagent Atomization

Location	**Project Status**	**Contaminants**	**Technology Type**
Marshall Space Flight Center	Monitoring/Inject	Trichloroethene	Chemical reduction
Technical Contact	**Project Dates**	**Media**	
Amy Keith Building 4200, Room 436 MSFC, AL 35812 Tel: 256-544-7434 Fax: 256-544-8259 E-mail: amy.keith@msfc.nasa.gov	Accepted 2001 Final Report	Low permeability clayey residuum	
	Costs Documented?	**Project Size**	**Results Available?**
	Yes		Yes

The information in this project summary is current as of January 2003.

1. INTRODUCTION

The Marshall Space Flight Center (MSFC) is located in northern Alabama within Redstone Arsenal (RSA). MSFC was listed with RSA on the National Priorities List on May 31, 1994. Past solvent management practices during the 1960 era of rocket engine testing at MSFC resulted in groundwater contaminated with chlorinated volatile organic compounds (CVOCs) beneath MSFC. Five major plumes with fourteen main contaminant source areas (SAs) have been identified at the facility. Source areas are those areas that have elevated concentrations of CVOCs in soil and groundwater that may act as the continuing source of contamination in the downgradient groundwater. MSFC is pilot testing in-situ technologies to identify the effective remedial technologies approaches for remediating the source areas. SA-2 and SA-12 were chosen for testing in-situ chemical reduction technology using pneumatic fracturing and the Liquid Atomized Injection® (LAI) injection process for delivery of a zero-valent iron (ZVI) slurry (Ferox®) to subsurface target zones. The results from these and other on-going or planned in-situ pilot tests (chemical oxidation, dynamic underground stripping, enhanced bioremediation, and phytoremediation) will be used to complete a CERCLA feasibility study for the groundwater medium at MSFC.

2. BACKGROUND

The subsurface beneath the area consists of a low-permeability clayey residuum overlaying karst bedrock. The majority of the contaminants are believed to lie within the basal layer of the residuum, called the rubble zone, that transitions into the underlying bedrock. The residuum groundwater, which is naturally aerobic, moves mostly in a lateral manner through the rubble zone to wetlands and springs downgradient. The degree of hydraulic connection between the rubble zone and the bedrock is variable throughout the site. Due to the complex hydrogeology of the site, only a few remediation technologies are expected to be effective at MSFC. After screening available technologies, in-situ chemical reduction was chosen for pilot-scale tests to treat dissolved trichloroethene (TCE) conditions in groundwater. SA-2 and SA-12 were identified for implementation of the in-situ chemical reduction treatability studies. The MSFC team included CH2M HILL as the prime contractor and ARS Technologies, Inc. (ARS) as their specialty technology subcontractor.

3. TECHNICAL CONCEPT

Chemical reduction using ZVI reduces TCE by reductive dechlorination where hydrogen ions are liberated by the corrosion of iron in water. TCE uptakes the hydrogen ion and releases a chloride ion, ultimately reducing TCE to dichloroethene, vinyl chloride, and ethene. The release of chloride ions can be monitored to measure the progress of the reaction process. The low-permeability residuum severely limits the amount and distribution of fluids that can be delivered. Pneumatically fracturing the residuum and atomizing the chemical reagents to be injected delivers increased quantities of the ZVI slurry and more evenly distributes the slurry within the matrix contamination. ARS uses nitrogen gas for fracturing and as an inert carrier during Ferox® injections, and incorporates a Liquid Atomized Injection (LAI) process to deliver fluids into the subsurface.

4. ANALYTICAL APPROACH

At SA-2, because of the presence of unexploded ordnance, the entire area with the highest levels of groundwater contamination could not be treated with the ZVI injections. To address the inaccessible areas, a downgradient treatment zone was created through overlapping injections, forming a permeable reactive zone to treat migrating untreated groundwater.

At SA-12, a 10-foot by 50-foot treatment cell was demarcated within the area of highest groundwater contamination. Subsurface intervals within the cell were pneumatically fractured and the ZVI slurry was injected into the reactive treatment zones to treat the highest contaminant concentrations (subsurface and groundwater media). The injection process allowed the ZVI placement to occur without damage to numerous subsurface utilities and structures in the highly industrialized area. DNAPL-like concentrations (about 500 mg/L) of TCE were unexpectedly encountered at a location within SA-12 after the field test implementation had begun.

5. RESULTS

At SA-2, 11,000 lbs of ZVI were injected achieving an iron-to-TCE weight ratio of 200:1. Follow-up sampling showed iron impregnation of the subsurface matrix. Pressure readings and field measurements for iron during Ferox® injection indicated that the radius of influence ranged from 20 to 60 feet. Groundwater conditions were changed from an aerobic, non-reducing state to anaerobic, reducing conditions. TCE concentrations were reduced from 72,800 ppb to 3,400 ppb (over 95% reduction) over the initial fourteen months. Monitoring continues and further reductions are expected.

At SA-12, 4,500 lbs of ZVI were injected achieving an iron-to-TCE weight ratio of 100:1. At SA-12 similar radii of influence and geochemical effects on groundwater conditions were observed as those at SA-2. Some reduction in TCE groundwater concentrations were observed initially, but the concentrations rebounded and remained fairly constant throughout most of the groundwater performance monitoring period. The low iron-to-TCE weight ratio and the lack of TCE degradation is attributed to the post-implementation discovery of the DNAPL-like TCE conditions. Supplemental bench-scale tests indicate that these types of conditions could be treated using ZVI and the effectiveness of additional injections at SA-12 is being considered.

6. HEALTH AND SAFETY

All field work is performed under a Health and Safety Plan to address all pilot study activities. All workers review the HSP before work begins at the site and it is maintained on site during activities. Each subcontractor must provide a HSP specific to the work they do. The plan includes project-specific physical hazards, project-specific chemical hazards, and emergency procedures. All personnel were HAZWOPER trained. The in-situ pilot tests have been implemented safely and without incidents, and the field implementation phases passed all internal health and safety audits.

7. ENVIRONMENTAL IMPACTS

Injection of ZVI into groundwater may change the pH, the dissolved oxygen, and the oxidation reduction potential (ORP) levels, and increase iron concentrations, within a localized area.

8. COSTS

The total cost for completing the SA-2 tasks listed below was approximately $300,000, incurred between 1999 and 2001:

- Work planning
- Soil and groundwater sampling
- Bench-scale testing and report
- Utility surveys and video-logging
- Fracturing and ZVI injections (including mobilization and demobilization)
- Royalty fees (related to pneumatic fracturing, patented by the New Jersey Institute of Technology)
- Development of field documentation report
- Technical support and project management

The amount of ZVI injected into the subsurface beneath SA-2 was 11,000 pounds. Therefore, the cost to implement the pilot test per pound of ZVI injected was $27.26, based on the total cost value. The actual field implementation portion of the test was approximately 70 percent of the total cost which corresponds to $19.06 per pound of ZVI injected.

9. CONCLUSIONS

In-situ chemical reduction using the Ferox® ZVI process is an effective method for treating dissolved phase TCE in groundwater, where DNAPL-like concentrations are not present. The use of ZVI for treating DNAPL or DNAPL-like conditions is a possibility, based on bench-scale results. The selective injection method is useful for treating areas with limited accessibility and ARS' LAI process, combined with pneumatic fracturing, is effective for delivering and distributing ZVI slurry in low-permeability media. Results at SA-12 also show that ZVI can treat Freon contamination in groundwater.

10. REFERENCES

1. Marshall Space Flight Center. Summary (Draft): In-Situ Chemical Reduction Pilot Test Results for Source Area 2. Prepared in consultation with CH2M HILL and ARS Technologies. September 2001.

2. Marshall Space Flight Center. Summary (Draft): In-Situ Chemical Reduction Pilot Test Results for Source Area 12. Prepared in consultation with CH2M HILL and ARS Technologies. September 2001.

Project No. 33			
Chemical Oxidation and Natural Attenuation at the Camden County Landfill			
Location Camden County, Georgia	**Project Status** First source area complete.	**Contaminants** Chlorinated ethenes	**Technology Type** Chemical oxidation and natural attenuation
Technical Contact Clifton C. Casey South DIV Naval Facilities Engineering Command Tel: 843-820-5561 Fax: 843-820-7465 E-mail: caseycc@efdsouth.navfac.navy.mil	**Project Dates** Accepted 2001 Final Report	**Media** Groundwater	
	Costs Documented? Yes	**Project Size** 120 ft x 40 ft	**Results Available?** Yes

Project 33 was completed in 2002.

1. INTRODUCTION

In-situ Chemical Oxidation (ISCO) and natural attenuation was used to reduce the source of a plume of chlorinated hydrocarbons and its residual concentrations in groundwater to meet regulatory cleanup goals. The strategy for this remedial action was to incorporate an aggressive approach to reducing the mass of contamination in the source area aquifer sediments followed by natural attenuation of the residual contamination in groundwater. The cleanup objective was to protect a nearby residential community from the plume of contamination that was moving offsite and meet state and federal regulatory cleanup goals for groundwater.

2. BACKGROUND

The site is a 25-acre municipal landfill that was operated by the County during the mid 1970's to 1980. A variety of wastes from the community and the Naval Base Kings Bay were disposed in the landfill. Wastes were disposed by the trench method wherein trenches were dug, backfilled with waste, and covered with fill. In the early 1990's, a RCRA Facility Investigation (RFI) identified groundwater contamination at the perimeter of the landfill. A perchloroethene (PCE) plume was determined to be migrating towards a subdivision located several hundred yards from the landfill. As an interim measure, the Navy installed extraction wells to hydraulically contain the plume at the perimeter of the landfill (Casey and Beregren, 1999).

Results of additional site investigations, determined that the PCE source was approximately 120 feet long by 40 feet wide in the 30 to 40 foot horizon below ground surface. In addition, PCE degradation products including trichloroethylene (TCE), cis-1,2 dichloroethene (DCE), and vinyl chloride (VC), were detected in the groundwater. Total chlorinated aliphatic compounds (CACs), the sum of PCE and its degradation products TCE, DCE, and VC, were detected at concentrations of more than 9000 micrograms per liter (µg/L) in the groundwater within the landfill source area. PCE concentrations were as much as 5 percent of the pure phase solubility phase, therefore, the presence of a dense non-aqueous phase liquid (DNAPL) was inferred.

An evaluation (Chapelle and Bradley, 1998) of the attenuation capacity of the aquifer determined that the plume was readily degrading naturally as it moved away from the source area. The geochemistry of the site indicated that the source area was sulfate reducing and the downgradient plume was an iron-reducing environment. These environments allowed for the highly chlorinated compounds such as PCE and TCE to be readily degraded to DCE and VC. The iron reducing environment downgradient was more ideally suited for the lower chlorinated compounds that can be anaerobically oxidized under these environments

(Bradley and Chapelle, 1996, Bradley and Chapelle, 1998). Modeling results indicated that if the concentrations of total CACs were reduced to 100 µg/L, natural attenuation would address the residual contamination, achieving compliance levels in the groundwater plume prior to reaching the facility's boundaries.

The cleanup approach incorporated the use of aggressive source reduction using chemical oxidation, followed by natural attenuation to degrade the residual concentrations in groundwater. Forty-four carbon steel injection points were located in and around the source of contamination. Injection of Fentons Reagent occurred in two zones starting on November 2, 1998. The primary treatment occurred in the source area and a follow-up treatment took place within 25 feet downgradient. The injections were completed on July 15, 1999.

3. TECHNICAL CONCEPT

In-Situ Chemical Oxidation using Fentons Reagent method was selected as the technology for source reduction. The process involved injecting a 50% solution of hydrogen peroxide with ferrous sulfate as a catalyst. Hydroxyl radicals formed by the reaction of the peroxide and catalyst are powerful, non-specific oxidants. Complete mineralization of the contaminants is assumed to occur within a few minutes. The final products of the reaction between the hydroxyl radicals and the contaminants are carbon dioxide, water and chloride.

Biotransformation at this site occurs primarily by a process of reductive dechlorination in the source area. This occurs due to indigenous microorganisms at the site that mediate an oxidation reduction reaction to obtain energy and growth. In this reaction, the chlorinated solvent acts as an electron acceptor, and a chlorine atom on the molecule is replaced with a hydrogen atom. Dissolved organic matter (DOM) from the landfill serves as the electron donor to drive the reaction. After chemical oxidation of the source area, the dissolved organic matter is replenished by upgradient DOM that moves into the treated zone.

4. ANALYTICAL APPROACH

Pre and post-injection characterization of monitoring and injection wells included analyses for volatile organic compounds. Carbon dioxide gas was analyzed during injection of the reagent to determine completeness of the oxidation.

The natural attenuation evaluation included analyses of dissolved oxygen, ferrous iron, sulfate, hydrogen sulfide, nitrate, nitrite, and molecular hydrogen as well as volatile organic compounds.

5. RESULTS

After two treatment phases of injections, the CACs in groundwater were reduced from approximately 9000 ppb to less than 100 ppb. These concentrations have remained below this value since completion of injections. The state of Georgia Department of Natural Resources nominated the project for the State Chamber of Commerce Environmental Excellence Award for which it won.

6. HEALTH AND SAFETY

During injection, the treatment area was secured such that only operation personnel were allowed onsite.

7. ENVIRONMENTAL IMPACTS

None

8. COSTS

The direct cost for ISCO was approximately $250,000. This costs does not include installation of monitoring or injection points nor pre or post-injection monitoring. The natural attenuation evaluation cost was $100,000.

9. CONCLUSIONS

After two years of treatment in the initial source area, the groundwater concentrations have remained below the 100 ppb total CAC target level. Downgradient the residual concentrations of the plume have continued to drop due to natural attenuation and are expected to completely degrade within five years.

10. REFERENCES

1. Casey, C. and C. Beregen, C. 1999. Chemical Oxidation, Natural Attenuation drafted in Navy Cleanup, Pollution Engineering, March 1999 Supplement.

2. Bradley, P. M. and F.H. Chapelle. 1996. Anaerobic mineralization of vinyl chloride in Fe (III)-reducing, aquifer sediments. Environmental Science and Technology 30-2084-2086.

3. Bradley, P.M., and F.H. Chapelle. 1998. Microbial mineralization of VC and DCE under different terminal electron accepting conditions. Anaerobe. 4:81-87.

4. Chapelle, F.H. and P.M. Bradley. 1998. Selecting remediation goals by assessing the natural attenuation capacity of ground-water systems. Bioremediation Journal 2:227-238.

COUNTRY TOUR DE TABLE PRESENTATIONS

ARMENIA

The information in this tour de table is current as of January 2001.

1. BACKGROUND

Twelve tail storages have been constructed in the Republic of Armenia at different years that accumulate some 300 M cubic meters of wastes from mining industry. Waste composition is conditioned by mineral combination of paragenetic minerals.

Existing economic situation in Armenia within the recent years prevents set-up of full control over the tail storages. Being complex hydrotechnical facilities tail storages are representing a permanent hazard and appear to be a reason for a calamity.

Due to the impact the natural and climatic conditions content of tail storages (mainly metals) is weathered, transferred and spread to the adjacent areas by causing irreversible impact on human health, environment, including fauna and flora and resulting in activation of desertification processes.

From this viewpoint conserved tail storages of Geghanush in the province of Syunik, and the tail storage of Akhtala in the province of Lori are mostly hazardous. These tail storages are located on densely populated and developed farming areas and cause huge damage to the environment and human vital activity by simultaneously contributing to desertification of lands exclusion of them from the lands of farming and other value.

The need to protect the tail storages proceeds from not only the fact, that it is necessary to minimize and neutralize their harmful impact on the environment and human health, but also from rational use of natural resources, since the latter contain big quantities of useful and rare metals that represent a material value and their use might contribute to the country's development. However, these tail storages are not re-processed due to a lack and high cost of adequate technologies. The tail storages (see Table 2) as objects of hazardous hydrotechnical calamity by their impact on the environment and human health are classified based on the following factors and effects:

Table 1: Classification of Tail Storages Based on Harmful Factors and Effects

#	Harmful factors and effects	Grading unit (point)
1.	Volume	1-3
2.	Number of population in the affected zone	1-5
3.	Lands located in the affected zone (quality, class)	1-5
4.	Operated	1-2
5.	Conserved	1-4
6.	Facility construction form—ferro-concrete	1
7.	Land dam	2
8.	Content of hazardous substances, elements %1m^2	1-5
9.	Content of useful metals %1m^2	1-5
10.	Level of dispersion	1-2
11.	Possibility to conduct measures to prevent hazardous impact	1-5

According to the mentioned indicators classification of tail storages as the highest risk centres are referred to in Table 3.

The storages of Geghanush in the province of Syunik and the storage of Akhtala in the province of Tavush are selected as storages representing high risk and requiring primary preventive works to be prepared and implemented.

Selection of these tail storages is conditioned by the following criteria:

1. The tail storages of Geghanush and Akhtala are located in densely populated areas. Towns of Kapan, Shamlugh, Akhtala, a number of villages and settlements are located within its affected zone.

2. Desertification processes have been activated within the affected zone of the tail storages of Geghanush and Akhtala, which has been resulted in total extinction of plants and continuation of land alienation phenomenon.

3. Geological conditions of establishing and formation of the Kapan copper and Shamlugh copper multi-metallic deposit, as well as content of harmful components in the Geghanush and Akhtala tail storages caused by technological failure of ore material re-processing, which exceeds by 8-10 times the indicators of the rest of the tail storages.

4. High percentage of useful metal content conditioned by the prerequisites mentioned in item 3, which should protected for the economic development in the country.

5. The geographic location and natural-and-climatic conditions of the Geghanush and Akhtala tail storages could contribute to the wash-up and dispersion of the tail storages, while in the case of a collapse the animal kingdom of Vokhchi and Debed Rivers would be extinct.

6. Further operation of the Geghanush tail storage is prohibited given the fact, that drainage-system facilities located in the tail storage to secure removal of stormwater are under high pressure and additional accumulations on the currently conserved galleries would result in an accident by causing great damage to the environment, to the residential houses in the town of Kapan and commercial facilities.

7. Operation of the Akhtala tail storage is possible only in the case if the drainage-system canal is reconstructed.

2. MEASURES AIMED AT MITIGATION AND NEUTRALIZATION OF HARMFUL IMPACT OF THE TAIL STORAGES

In order to minimize hazardous impact of the tail storages generated due to the mining industry production activity it is necessary to conduct recovery and reclamation of the storage surfaces.

A tail storage or slurry field of each non-ferrous metallurgy-concentrating mill are former landscapes, which appeared to be under a layer of toxic substratum of chemical substances. Meanwhile, production wastes are fully eliminating natural fertile lands and fruitful biocenosis and new neo-landscapes of technological origin that lost their original economic and social values are spontaneously generated that leads to desertification.

All the prerequisites generate a necessity to conduct land reclamation, which includes a number of engineering, reclamation and biological measures to set-up fruitful land-and-plant landscapes.

In order to mitigate and neutralize harmful impact of the conserved tail storage of Geghanush in the province of Lori and tail storage of Akhtala in the province of Tavush it is necessary:

1. To arrange and carry out a periodical wetting system for tail storage surfaces layers and to sow perennial plants.
2. For that purpose it is necessary to select a method for artificial raining of the whole tail storage area. Water used for artificial raining could be procured both by gravity and pumping methods.

3. To cover (encircle) the whole surface of the tail storage by a liquid of polyacrylamide. The advantage of this method is, that polyacrylamide is gradually being hydrolysed by generating polycrylacidic ammoniac brine, which changes the structure of land surface layer by strengthening it and simultaneously remaining transparent for air and water and creating favourable enough conditions for regular growth of plants.
4. As a temporary measure to strengthen the tail storages surface land layer by means of special machine equipment to prevent shift of surface land layer under wind impact.
5. To reconstruct and repair drainage-system facilities surrounding the tail storages in order to prevent transportation of wastes from the Geghanush and Akhtala tail storages to other areas through river waters and generation of new desertification centres.
6. To cover the tail storage surface by a 10-15 cm-thick land layer and sow perennial grass plants.

Financial-and-economic calculations and cost estimation for the implementation of mitigation and neutralization measures of harmful impact of the tail storage of Geghanush in the province of Syunik and tail storage of Akhtala in the province of Lori should be refined by a competent designing organization taking into account peculiarities of local natural-and-climatic conditions, location of tail storages, availability and quantity of surface waters, feasibility studies of invested measures, etc.

The measure of covering the tail storage by a 10-15 cm-thick land layer is not observed by the financial and economic calculation, since it requires large-scale land works that would deteriorate the landscape natural balance.

In order to prevent harmful impact of the tail storages on the environment it is considered reasonable to input combined measures with the following essence.

The tail storages surface is preliminary processed by polyacrylamide. Then a wetting system for the surface land layer is constructed and afterwards perennial plants are sown.

Table 2: Classification of Tail Storages Located on the RoA Territory

#	Tail storage title and location	Year of putting into operation	Year of conservation	Volume M m^3	Particles average diameter	Waste content
1.	Right-bank tributary to Vokhchi River, Village of Darazam	1953	1961	3	0.067	Mo Cu SiO_2 Al_2O_3 MgO CaO TiO_2 FeO Na_2+K_2O P_2O_5 S Zn Pb rare metals
2.	Right-bank tributary to Vokhchi River, Village of Pkhrut	1958	1969	3.3	-"-	
3.	On Vokhchi River	1962	1977	30	-"-	
4.	On Artsvanik River	1978	Working	210	-"-	
5.	On Geghanush River	1961	1989	4.6	0.084	
6.	On Davazam River	1957	1977	30	0.087	
7.	In gorge No. 1 of Agarak	1978	Working	9	-"-	
8.	In gorge No. 2 of Agarak	1979	Working	17	-"-	
9.	In gorge No. 3 of Agarak					
10.	On Nahatak River nearby settlement of Akhtala	1971	1988	3.2	0.082	
11.	Nearby Village of Arazap (Province of Ararat)	1982	Working	20	0.085	
12.	On the right-bank of a tributary to the Nazik River nearby Settlement of Dastakert	1960	1968	3.1	-"-	

Table 3: Assessment of Hazardous Impact of the Tail Storages

Tail storage title and geographic location Characteristics (point)	Right-bank tributary to Vokhchi River, Village of Darazam	Right-bank tributary to Vokhchi River, Village of Pkhrut	On Vokhchi River	On Artsvanik River	On Geghanush River	On Davazam River	In gorge No. 1 of Agarak	In gorge No. 2 of Agarak	On Nahatak River nearby Settlement of Akhtala	Nearby Village of Arazap (Province of Ararat)	On the right-bank tributary to Nazik River nearby Settlement of Dastakert
Volume	1	1	2	3	1	2	1	2	1	2	1
Population in the impact zone	2	2	2	2	5	1	1	2	5	5	1
Lands in the impact zone	2	2	2	4	5	2	2	2	4	5	2
Working, non-working	3	3	3	1	3	1	1	1	3	1	3
Form of facility	1	2	2	1	4	2	1	1	4	1	2
Availability of hazardous substances	2	2	3	3	5	2	2	2	5	5	1
Availability of useful metals	2	2	3	3	5	2	3	3	4	1	4
Dispersion rate	2	2	2	2	1	1	1	1	1	2	1
Possibility to conduct measures to prevent harmful impact	2	2	3	1	5	2	1	1	4	3	3
Total	17	18	20	20	34	15	13	15	31	25	18
Degree of hazard	2	2	2	2	1	3	3	3	1	1	2

AUSTRIA

The information in this tour de table is current as of January 2002.

1. LEGAL AND ADMINISTRATIVE ISSUES

Austria has had a Federal Act for the Remediation of Contaminated Sites (ALSAG) since 1989. The main focus of this act is to provide federal funds for the clean-up of the most dangerous contaminated sites in the country. The fund is created through a tax on landfilling. The amount of waste tax depends on the technical standard of the landfill. Hence, landfills with a low standard have to be either adapted to the high standard defined in the Landfill Ordinance, or closed by 2004 the intake of waste tax will decrease. At present, the Federal Ministry for Agriculture, Forestry, Environment and Water Management (BMLFUW) is working on an amendment on ALSAG which will regulate the waste tax intake on a new basis. Additionally, the current and future use of the site should play a more important role when remediation goals are defined and the polluter-pays-principle will be strengthened in the amendment.

In order to support sound decision making, the Austrian Standards Institute has published a standard on “Contaminated Sites – Risk Assessment Concerning the Pollution of Soil” in spring 2000 and has started to work on a standard on “Contaminated Sites – Risk Assessment Concerning the Pollution of Soil-Air.”

2. REGISTRATION OF CONTAMINATED SITES

The BMLFUW registered 2.499 suspected sites. So far, the major part relates to abandoned landfill sites because their data and registration are easily available. Detailed risk assessments showed that 148 sites pose a considerable risk to human health or the environment and therefore were classified as contaminated sites.

Currently, the work of identification of potentially contaminated sites focuses on industrial sites in Upper and Lower Austria.

Remediation projects for registered contaminated sites are funded via the Kommunalkredit Austria AG on behalf of the Federal Ministry BMLFUW. So far, 110 remediation projects, with a total cost of EURO 340 mio. (approximately 200 mio. US$) were funded.

3. TECHNOLOGY DEVELOPMENT PROGRAM

In 2001, the BMLFUW issued a concept on research priorities to tackle contaminated land problems in Austria. Currently, an initiation of a Center of Competence is under development which will guide and co-ordinate future research activities. All these initiatives will stimulate technology development in Austria.

4. REMEDIAL METHODS IN USE

“Safeguarding” Methods:	Number
capping of landfill	29
extraction of landfill gas	11
enclosure	32
hydraulic measures	38
pump and treat	20
in-situ sorting of material	9

Remediation Methods:	Number:
excavation off site	24
groundwater remediation	11
soil vapor extraction/bioventing	18
bioremediation	2
soil washing	4
thermal treatment	4
biological treatment	4
immobilisation	4

5. RESEARCH AND DEVELOPMENT ACTIVITIES

The Austrian Environment Agency has been the coordinator of the EU Concerted Action CLARINET (1998-2001). This project has been one of the main R&D initiatives on contaminated sites in Europe. Further information can be obtained from the CLARINET website at http://www.clarinet.at.

BELGIUM

1. LEGAL AND ADMINISTRATIVE ISSUES

A. Background Information

The Belgian Constitution dividing the authority between the Federal State and the Regions, confers the responsibility of environment protection policy almost exclusively to the three Regions: Flanders, Wallonia and the Brussels-Capital Region, with very limited exceptions.

This means that there cannot be such thing as a federal legislation on soil protection, nor any federal strategy in this matter. As long as Europe does not enforce a common framework to all Members States, the three Regions are free to legislate or not, in this issue, according to their own policy, the requirements of their citizens, and the constraints of their economy.

However, contacts have been initiated in 2001 between the three Regions in order to see to what extent the three soil policies (the Flemish one, already enforceable, and the two others, in preparation) could be harmonized. These works have led to a first draft report where common norms (trigger values/clean up values) for groundwater are proposed.

B. Summary of Legislation

Until now, only **Flanders** has adopted a full legislative framework for contaminated sites. The main characteristics of the Flemish Decree on Soil Remediation, adopted in 1995 and brought into force in different stages, were presented in previous NATO/CCMS Pilot Study meetings. Its guiding principles are the registration of all contaminated or suspected sites, the distinction between duty and liability, and the distinction between historical and new soil contamination.

Soil remediation standards and background levels have been adopted by the Flemish Government. The soil remediation standards depend on future land use. Exposure scenarios have been defined for four land use classes (agricultural, residential, recreational and industrial). Plus nature areas, requiring a separate approach.

There is also a list of activities which could create soil pollution, and need to be investigated by transfer of property or closing of activity.

In **Wallonia**, the present legislation is based on a Waste Decree and on Town and Country Planning provisions. In addition, Wallonia has the oldest legislation in Belgium – and one of the oldest in Europe – dealing specifically with brownfield issues: the Act of 1978 on the restoration of disused economic sites, amended in 1997 and included in the Walloon Planning Code.

In **Brussels-Capital Region**, a global legislative ordinance on soil remediation is still lacking, but soil and groundwater investigations and remediation can be asked for in some cases, based on the ordinance on environmental permits and the ordinance on the enforcement and prosecution of environmental criminal acts.

Since 1999, **Brussels** and **Wallonia** have also adopted special regulations for gas stations: these include control measures (soil and groundwater) and remediation procedures, according to soil standards and intervention values in relation with the land uses authorized in the surrounding area. Those regulations apply to all kind of situations: closing establishment, new establishment, license renewal or transfer, suspicion of pollution, etc. In addition, they impose a strict calendar for the control and eventual renovation of all existing gas stations.

Subsequently, a principle agreement between the three Regions, the oil companies and the Federal Government has been adopted, providing for the creation of a common Fund for the remediation of gas stations. The Fund will be financed on equal basis by the oil companies and the consumers, through a special levy.

Last but not least, the **Walloon Government** has launched a Strategic Programme for Contaminated Soils and Brownfield Sites, including the preparation of a comprehensive Soil Decree. This programme, which started in 2000, should be presented to the Walloon Parliament for a first lecture by the end of this year, after hearings involving all public and private stakeholders.

During the present transitory period, special measures will enhance the rhythm of brownfield sites reclamation, provide new means for a thorough updating of existing inventories of derelict and brownfield sites, and for preliminary investigations of these sites.

C. Administrative Aspects

For institutional reasons (see § 1.a), there is no Federal Agency for the Environment:

- In the Flemish Region, OVAM (Public Waste Agency of Flanders) is the responsible authority for soil control and remediation.
- In Brussels-Capital Region, the responsible authority is the Brussels Institute for
- Environmental Management.
- In Wallonia, as long as no decree on soil remediation has been passed, responsibilities are shared between various bodies: the Walloon Waste Office is the responsible authority for landfills and other polluted sites, according to the Waste Decree; the Town and Country Planning Administration is responsible for derelict land and brownfield sites.

The transitory measures adopted by the Walloon Government enhance the role of SPAQuE (the Public Society for the Quality of Environment) in the whole procedure, from inventory to remediation and aftercare; SPAQuE will also be in charge of the preliminary investigations of sites listed in the new inventory.

"Clean" or very slightly polluted sites will then be redeveloped under the authority of the Town and Country Planning Administration, while contaminated sites will be transferred to SPAQuE, for thorough characterization and subsequent reclamation on the basis of the Waste Decree.

2. REGISTRATION OF CONTAMINATED SITES

Flanders:

According to the legislation, a soil register has been created by OVAM in 1996. The Flemish authorities proceed with a systematic examination of potentially polluted areas mainly on three occasions:

- at the time of property transfer;
- at the closure of licensed installations; and
- whenever the license has to be renewed.

According to OVAM's Remediation Service (situation mid 2001), the descriptive investigations already carried out result in approximately 3000 lots of ground where a soil remediation project is needed (amongst these, 624 remediation plans are approved, and cleanup is going on or finished on 308 sites).

All information on soil pollution is compiled in the soil register, which serves as a data base for policy decisions and also as an instrument to protect and inform potential land purchasers.

A "soil certificate" is requested for all sorts of property transfers. This system has increased the number of voluntary investigations, and sometimes induces voluntary remediations, in order to avoid to be listed as contaminated in the register.

Wallonia:

A registration system has existed since 1978, based on the special brownfield legislation and aiming at the redevelopment of those sites. It takes into account more than 2.000 sites, covering 9.000 hectares of derelict land. The transitory measures (see § 1.b) have allowed not only to implement a general updating of this registration procedure, but also to enlarge its scope and provide new means for the investigations. These will rely on the hazard ranking system "Auditsol", developed by SPAQuE .

For the sites polluted by waste, the Walloon Waste Office holds an additional list of sites for which a remediation plan should be prepared, has been approved, or is into execution (more than 900 sites registered today).

Brussels Region:

The Region is currently setting up an inventory of all polluted sites. Results are expected by the end of September 2002. The conclusions will be used to develop a strategy for soil remediation in the Brussels region.

3. REMEDIAL METHODS IN USE

Until recently, there have been no comprehensive statistics on remedial methods and technologies used for clean-up in Belgium. The following soil and groundwater remediation techniques are available and used:

- Excavation and transport of contaminated material to a deposit site and/or processing of the contaminated soil.
- Hydrodynamic methods, by means of drains, water remediation, processing of slurry, etc.
- Use of degassing systems.
- Use of isolation techniques (horizontal and vertical isolation by means of cement, clay, bentonite, bitumen, etc.)
- Immobilization techniques by means of cement, lime, absorption methods for oil, etc.
- Remediation technologies: microbiological remediation, in-situ and ex-situ (landfarming, biopiles, etc.), water and chemical extraction, flotation, thermal treatment, steam-stripping, a combination of physico-chemical (soil washing and fractionation) and biological remediation techniques, electro-reclamation, infiltration and wash out, Permeable Reactive Barriers (PRBs), chemical oxidation.

4. RESEARCH AND DEVELOPMENT ACTIVITIES

For soils contaminated with heavy metals and metalloids, the following remedial techniques are in research and/or anticipated for use in the coming years:

1. In-situ immobilisation by means of soil additives.
2. Bio-extraction of heavy metals by means of micro-organisms in a slurry-reactor.
3. Phyto-extraction by means of plants with increased capacities of metal-accumulation.
4. In-situ bioprecipitation of heavy metals by sulfate reducing bacteria.

More generally, there is a great need and expectation for low-energy, cost-effective remedial technologies. Research is progressing in the Universities and Public research Institutes, mainly in microbiology and phytoremediation areas, although no comprehensive evaluation is yet available.

VITO (The Flemish Applied Research Institute) is currently engaged in the following R&D activities:

1. Inorganic reactive barriers (zero valent iron): treatability studies, material selection, circumventing clogging, protocol development for design, installation and monitoring, quick screening test for zerovalent iron quality, slow screening test for zerovalent iron efficiency testing;
2. Biological permeable reactive barriers and permeable barriers for mixed pollutions (Multibarriers);
3. Circumventing bio-availability limitations for bioremediation of PAH and mineral oil;
4. Developing protocols for monitoring of natural attenuation, in-situ bioremediation and pump & treat remediation as well as field monitoring for these technologies;
5. Phytoremediation;
6. Bioremediation of TNT;
7. BTEX-biodegradation (autotrophic conditions);
8. Biodegradation in NAPLs;
9. Remediaton of gasmanufacturing plants (PAHs, heterocyclic compounds, cyanides etc);
10. MTBE biodegradation by using ORCs;
11. TCE biodegradation by using HRCs;
12. BTEX biodegradation by using ORCs;
13. Influence of compost on biodegradation processes and chemical analysis;
14. Sorption barriers for heavy metals;
15. In situ redox manipulation;
16. Oil characterisation methods;
17. Biodegradation of VOCLs;
18. Chemical oxidation tests;
19. Natural attenuation and in situ microcosms; and
20. Natural attenuation at the interface (groundwater – surface water)

5. CONCLUSIONS

There has been recently a growing recognition of soil and groundwater contamination issues in Belgium. In the Flemish Region, the implementation of the Soil Decree has a highly positive influence on soil management and soil environmental quality. Forthcoming months will show new developments in Wallonia, and maybe in Brussels.

The problems we are tackling now are:

- the lack of ressources of many liable parties, for the cleanup of historical pollution;
- the need to improve the cost-efficiency and environmental merit of the remediation programs, whether funded by public or private money ; and
- the difficulty in matching stringent soil regulations with the necessity of redeveloping brownfield sites, in a sustainable land use strategy.

This last point might become, in the near future, the most difficult issue to cope with.

CANADA

Please Note: The following provides an update of the Tour de Table presented on Canada's contaminated land activities at the meeting in Wiesbaden, Germany (Annual Report 2000 Number 244). Unless otherwise stated, the reader should assume that information is unchanged from the 2000 Report.

1. LEGAL AND ADMINISTRATIVE ISSUES

Protection of lands and water in Canada are generally covered under one or more of the three federal Acts namely the Fisheries Act[1], renewed Canadian Environmental Protection Act [2] 1999 and Canadian Environmental Assessment Act[3]. Most of Canada's 10 provinces and 3 territories have established their own statute or regulations with guidelines, policy or other criteria specific to contaminated sites management. A policy framework for federal contaminated sites is nearing completion. It will comprise a suite of policies, best practice advisories, and references to ensure that departments take a sound environmental stewardship approach to federal real property and to ensure that federal contaminated sites are managed in a consistent and systematic manner while recognizing the principle of risk management.

Federal responsibility for contaminated sites is acquired through the direct actions and operations of the government, or ownership of sites contaminated by others, and through other obligations such as Aboriginal Land Claims. There is a concern that the federal government's potential litigation costs related to this issue is increasing. There is also a growing recognition that conventional mechanisms for resolving disputes, such as litigation are not ideal for managing contaminated site issues. Other approaches such as Alternative Dispute Resolution (ADR) are currently being investigated as an option for encouraging participatory resolution to these issues.

2. REGISTRATION OF CONTAMINATED SITES

A complete inventory of contaminated sites in Canada does not exist. The number, however, is likely in the neighborhood of 23,000 with an associated remediation cost of around $16 billion. 60% of these sites are believed to be contaminated with petroleum hydrocarbons and over 10% are believed to fall under the sub-set known as Brownfield's. The federal government is currently compiling an inventory of contaminated sites for which it is responsible as well as an estimate of its associated liability. In 1996, the Auditor General of Canada estimated that there 5,000 such sites with an estimated liability of $2B. This number, however, is now thought to be overestimated. Current spending on federal contaminated sites averages $Can 120M per year.

The Canadian Council of Ministers of the Environment (CCME)[4]

The Canadian Council of Ministers of the Environment is the major intergovernmental forum in Canada for discussion and joint action on environmental issues of national and international concern. It comprises environment ministers from the federal, provincial and territorial governments.

In October 1989, the CCME initiated a five-year, $250M (50% federal) National Contaminated Sites Remediation Program. Although this program resulted in the remediation of several sites and the development of many tools and guidelines that are still in use today, the health and environmental risks associated with contaminated sites remains a priority to Canadians. Documentation related to many of these tools and other publications related to contaminated sites can be found on the CCME website[4]. The following is a list the more commonly used documents:

1. National Classification for System (NCS) - A method for evaluating contaminated sites according to their current potential adverse impact on human health and the environment. The system was developed to establish a rational and scientifically defensible method for comparable assessment of contaminated sites across Canada.

2. National Guidelines for Decommissioning Industrial Sites - A logical step-by-step approach to develop decommissioning and cleanup guidelines that are compatible with the intended land use future land use by eliminating human health concerns and mitigating environmental effects.
3. Guidance Manual for Developing Site-specific Soil Quality Remediation Objectives for Contaminated Sites in Canada - Recommended specific procedures for deriving remediation objectives for soil using the guideline-based approach. These recommendations include procedures for evaluating the applicability of the generic guidelines to individual contaminated sites and for modifying these guidelines to account for atypical or unique site characteristics.
4. Canadian Environmental Quality Guidelines (updated 2001) - Science-based goals for the quality of atmospheric, aquatic, and terrestrial ecosystems. They are national benchmarks or indicators of environmental quality and are normally used as a trigger to indicate that further investigation is required at a site. Although these guidelines are nationally endorsed and generally applied to federal contaminated site, provincial and territorial jurisdictions may have their own assessment tools (e.g. criteria, guidelines, objectives and standards), which may be implemented within their respective jurisdictions.

Canada-Wide Standard for Petroleum Hydrocarbons In Soil[5]

Petroleum Hydrocarbons (PHC) is one of six priority substances addressed under the Canada-wide Standards (CWS) sub-agreement of the 1998 Federal-Provincial Harmonization Accord of the CCME. On May 1, 2001, all jurisdictions except Quebec endorsed the CWS for Petroleum Hydrocarbons in Soil. Although Quebec did not sign the agreement that led to the standards, it shall remain committed to act within its area of jurisdiction in a manner consistent with the standard. The PHC-CWS sets out the national levels to which soil must be cleaned when sites contaminated by fuels or lubricants are subject to remediation.

Brownfields

Brownfields are commonly known in Canada as “idle or underused properties where past activities have caused environmental contamination but which nevertheless provide economically viable business opportunities”. These sites are mainly located in established urban areas, where existing municipal services are readily available, or along transportation corridors. Interest in the redevelopment of Brownfield’s in Canada is increasing at all levels, specifically in large urban areas such as Toronto, Montreal and Quebec City. The provinces of Ontario and Quebec have been particularly active in this area for the past few years with Ontario’s recent regulation and Quebec’s redevelopment initiatives and the Montreal Centre of Excellence for Brownfield’s Restoration (MCEBR). The National Roundtable on the Environment and the Economy (NRTEE), an independent advisory body on promoting sustainable development, with members appointed by the Prime Minister of Canada, has also been actively raising the profile of this issue. The Roundtable is currently leading the development of a national strategy for Brownfields in Canada, which is expected to be released in the fall 2002.

Orphaned /Abandoned Mines Sites

The negative health and environmental impacts caused by orphaned/abandoned mine sites is increasingly becoming a concern in Canada. In September 2001, the Mines Ministers agreed to a series of recommendations and guiding principles to address the issues related to these mine sites. The Ministers also agreed to establish a multi-stakeholder advisory committee to implement the recommendations and to report back to the Mines Ministers in September 2002. This initiative includes, among other recommendations, capacity development for a national inventory of these sites, development of a plan to foster community involvement in decision-making about closure and reclamation standards, as well as a plan for sharing responsibility and stewardship where ownership cannot be established.

3. REMEDIAL METHODS IN USE

Canadian contaminated sites generally fall under the following key categories:

- Formerly unregulated disposal sites;
- Industrial properties - spills, leaks, open storage areas, fill areas;
- Electrical facilities - PCB leaks and spills;
- Fire-fighter training areas;
- Ports and waterways where past industrial discharges contaminated sediment;
- Lagoons used to store or "treat" industrial effluents;
- Mine tailings ponds;
- Municipal and industrial landfills;
- Military training areas; and
- Wood preserving sites.

In Canada, the application of traditional "low-tech" technologies still remains the general trend due to undesirable climate conditions in the North, large hauling distances, low tipping fees and high availability of land. Although this is the trend, R&D, demonstration and application of innovative technology combinations and enhancements to existing technologies is making progress. Examples of recent innovative technology applications include the use of combinations of new or existing technologies such as two-phase partitioning bioreactor and bioreactor/biopile technology to treat PCB contaminated soil, in-situ bioslurping and thermal for the removal of petroleum hydrocarbons, phytoremediation for polishing/low concentrations of mix organic and inorganic contaminants, biofiltration of effluents from a bioslurping operation, as well as several others.

A webpage is currently under development, which will provide links to information related to contaminated sites in Canada. Areas of focus will include: access to databases and documentation on remediation technologies and technology providers; linkages to research institutes/organizations; funding programs; case studies and other focus areas related to contaminated site management. This webpage is expected to be finalized and posted to the Government of Canada website by the end of 2002.

4. CONCLUSIONS

As described above, contaminated sites remain an issue of concern for Canadian governments, the private sector and the public. Responsible parties have made significant progress on the assessment and remediation of their contaminated sites and continue to see this issue as an important environmental challenge.

5. REFERENCES

The following list of web sites and publications are currently available at the listed sites or in hard copy. In the future, these sites will be accessible directly through the Contaminated Sites Web page referred to in the summary above.

1. www3.ec.gc.ca/EnviroRegs/Eng/SearchDetail.cfm?intAct=1017- web page describing the Fisheries Act. The Minister of the Environment has the responsibility for administration and enforcement of subsection 36(3) of the Fisheries Act, which deals with the deposit of deleterious substances into water frequented by fish.

2. www3.ec.gc.ca/EnviroRegs/Eng/SearchDetail.cfm?intAct=1001- Webpage describing the Canadian Environmental Protection Act (CEPA) 1999. The goal of this renewed Act is to contribute to sustainable development through pollution prevention and to protect the environment, human life and health from the risks associated with toxic substances. It acknowledges the need to virtually eliminate

the most persistent toxic substances that remain in the environment for extended periods of time before breaking down bioaccumulative toxic substances that accumulate within living organisms.

3. www3.ec.gc.ca/EnviroRegs/Eng/SearchDetail.cfm?intAct=1000 - web page describing the Canadian Environmental Assessment Act. The Act requires federal departments, including Environment Canada, agencies, and crown corporations to conduct environmental assessments for proposed projects where the federal government is the proponent. It also requires environmental assessments when the project involves federal funding, permit or license.

4. www.CCME.ca - Site describing the activities carried by the Canadian Council of the Ministers of the Environment, the major intergovernmental forum in Canada for discussion and joint action on environmental issues of national and international concern

5. www.ec.gc.ca/CEPARegistry/notices/NoticeText.cfm?intNotice=54& intDocument=363 Canada-wide Standard on Petroleum Hydrocarbons in Soil

6. www.ec.gc.ca/etad/csmwg/index_e.html - Site providing up-to-date information on the activities carried out by the Federal Contaminated Sites Management Working Group. This committee, an interdepartmental technical working group, promotes a coordinated approach in the management of federal contaminated sites in Canada.

7. www.ec.gc.ca/etad/csmwg/workshop_e.html Innovative Site Assessment and Remediation Technology Workshop for Federal Contaminated Sites, November 2000

Recent Publications of Interest (Not yet posted on the above websites):

1a. Federal, Provincial and Territorial Framework for the Management of Contaminated Sites in Canada, Final report, LJM Environmental Consulting, October 2001.

1b. Federal, Provincial and Territorial Framework for the Management of Contaminated Sites in Canada, Final Report –Tables, LJM Environmental Consulting, October 2001.

2. Compilation and Review of Canadian Remediation Guidelines, Standards and Regulations, SAIC Canada, January, 2002.

CZECH REPUBLIC

The information in this tour de table is current as of January 2002.

1. INTRODUCTION

At the previous meetings of the Pilot Study, the legislation background and administrative procedure of remediation of environmental damages caused by the former Soviet Army and remediation of the polluted sites in the course of privatisation have been fully described.

From 1990-2000, the amount provided from the state budget for study and decontamination work on the previous Soviet military bases, including risk analysis and supervision reports, equalled approximately 1 118 mil. CZK. It is expected that it will be necessary to expend a further 320 - 370 mil. CZK by 2008. This year, the clean-up continues on six sites and two tenders are intended to be called for the supplier of the remedial action (chlorinated hydrocarbons in groundwater in area of previous military laundry and site with free oil phase on groundwater level). Total expenses in 2001 should be 75 mil. CZK.

In the course of privatization, some principles of reimbursement of environmental obligations by the National Property Fund was modified by the Resolution of the Government of the Czech Republic No. 51/2001, *On Principles of Settlements of Ecological Obligations Originated before Privatization,* which amends Resolutions No. 123/1993 and No. 810/1997. Important new principles are following:

- the order of remediated sites will reflect priorities assessed by Ministry of the Environment with respect to their risk on health of human beings and/or ecosystems;
- consent of the Government for the National Property Fund to make an Ecological Liability Agreement with new owner of the privatised property has effectiveness only two years;
- in the case of serious ecological threat due to pollution of groundwater or soil in privatised enterprises the Ecological Liability Agreement can also be made in cases that the Project of Privatisation was submitted before the 1 March 1992 in spite of an absence of Eco-audit in the project. Obligatory conditions are the risk analysis to prove serious threat and recommendation of the Ministry of the Environment;
- The National Property Fund is authorised to reimburse expenses of prospections, risk analysis and their bringing up-to-date, making projects, remediation of polluted soil, groundwater and building constructions, supervisions and pilot studies in the case of new unattested technologies;
- the Ecological Liability Agreement can be terminated after the remediation measures, imposed by the Czech Environmental Inspection (CEI), was reached what must be confirmed by CEI.

In the period from 1991 to 31 December 2000, the Government of the Czech Republic confirmed 257 agreement guarantees of the National Property Fund, in an amount of 139.233 billion. CZK; of this number 240 Environmental Liability Agreements were concluded. The expenses paid until now for remedying historical burdens on the privatised property by the National Property Fund were as follows: 1993 - 9.1 mil. CZK, 1994 - 139.2 mil. CZK, 1995 - 817.7 mil. CZK, 1996 - 949.7 mil. CZK, 1997 - 1 375.3 mil. CZK, 1998 - 2 173.6 mil. CZK, 1999 - 1 758.9 CZK, 2000 - 2 129 mil. CZK. Remediation activities were finished at 17 sites, 89 cases are continuing. Until now, the greatest remedy is former coking plant Karolina in the centre of the town Ostrava where more than 500 000 tons of soils polluted by coal tar is remediated by the technology of thermal desorption (supposed expenses over 1.7 billion CZK).

2. LEGAL AND ADMINISTRATIVE ISSUES

Meanwhile, the reimbursement of expenses of remedying historical environmental damages by the National Property Fund is not subject of the process of approximation of the Czech Republic to the European Union, the amendments of several Acts important in protection of the soil and groundwater which were enacted during the last year are, at least in part, result of the harmonisation and implementation of the environmental legislation of the European Communities to the Czech Republic.

The Water Act No. 254/2001 will come into force on 1 January 2002. The polluter-pays principle accepted in the previous version has been used here also. Obligation to remedy contaminated surface and ground water respectively has been, however, imposed to the owners of the privatised property in spite of the fact that they are not polluter if they were informed about these ecological damages or the price of the property was reduced due to high probability of environmental damages at the site**.** For the purposes that remedial measures cannot be imposed on polluter or on the owner of property, and there is a threat of serious deterioration or pollution of surface or ground water, the water management authority shall establish a special account within its budget which will be supplemented annually to maintain the balance of CZK 50,000,000.

In the field of the waste management the clean-up and reclaiming of landfills that have been closed by law is a serious financial problem. Since 1996 only technically secured landfills have been in operation in CR. Landfilling of waste highly predominate, only about 2 % of waste were incinerated. A new Act No. 185/2001, on Wastes, which will come to force on 1 January 2002, is fully compatible with EU regulations. All the necessary implementation regulations are close to completion.

Act No.66/2000 on Geological Works has included determination and elimination of anthropogenic pollution in the geological environment (rocks, soils and groundwater) as part of geological works. Consequently, the planning, carrying out and assessment of clean-up works may be carried out only by legal and natural persons who fulfil the conditions laid down by the legal regulations ("an organisation") and in which there is a person with certificate of professional qualification to plan, carry out and evaluate remedial actions who is responsible for the management and evaluation of such work.

The requirements of the EC Air Protection legislation will be covered by the new Clean Air Act and its implementing Decrees. This legislation will come into force in November 2001.

The most important with respect to the topic of this meeting is preparation of the draft of new Act on identification of chemical environmental burdens in groundwater, soil, rocks, and building constructions and their remediation. Previous legislative background was concentrated on remediation of historical contamination in process of privatization of the state enterprises. This new law will implement risk based contaminated land remediation and management duty on broad range of land owners who use or used pollutant listed in the appendix of the law. The law proposal should be submitted to the Government and Parliament next year and is expected to be in force in 2003.

Following regulations for the remediation of contaminated sites are a substantial part of the draft:

1. each owner of property in which harmful chemicals listed in appendix of the Act are used and each owner of land with landfill owe the duty to make prospection of the site for these chemicals in groundwater, soil, and building constructions;
2. ascertained concentrations of the chemicals are compared with control standards (control standards: A level - background; B level - approximately the average between A and C levels; C level - concentration which may be harmful if this control standard is exceeded, different C levels for soil are given according to type of land use);
3. owner of the property in which control standard A are exceeded and risk analysis prove an unacceptable risk for individual humans or ecosystems owe the duty made remediation of the site to the target concentration levels assessed by regional authorities or by Czech Environmental Inspection;
4. in the case that duty of remediation is assessed the owner owe the duty to effect insurance against loss and damage due to environmental burdens. If the insurance is not effected the owner owe the duty to build up financial reserve;
5. if remediation cannot be realised to the target limits due to the lack of proper technology of if expenses are too high and inadequate to the health risk decrease, compensatory measure can be assessed by CEI. Compensatory measures have form of financial dues.

3. BROWNFIELDS

The Ministry of the Environment, as the highest body of the environmental state administration, bears responsibility in preparing and implementing state policy in the sector of Brownfields. In *The State Environmental Policy of CR, 2001,* the necessity to prevent further investments in "green-field" construction. There is not, however, any unified approach to the brownfields despite the fact that the statistics continue to show an ongoing delpetion of greenfields in the Czech Republic in recent years. Many of the polluted sites remediated in the frame of the privatisation process or as historical burdens after the former Soviet Army is possible to consider as Brownfields. The first attempt at recovery of unused territory is being implemented in the historical centre of the coal mining and iron works - in the region of town Ostrava with the support of US EPA. The Welsh Development Agency has elaborated study "A strategy for industrial land reclamation in the Czech Republic".

The MoE (Department of Environmental damages) provides support for 2 projects: 1) Integration of information on landfills and contaminated sites from the past and their risk assesment, and 2) Analysis of toxic intermediates of polyaromatic hydrocarbons biodegradation. These projects are payed from the research and development fund.

FINLAND

The information in this tour de table is current as of January 2002.

1. LEGAL AND ADMINISTRATIVE ISSUES

A. Soil Protection

The new Environmental Protection Act (86/2000) – which entered into force 1.3.2000 – implemented the IPPC directive (96/61/EC). Environmental Protection Act (EPA) is a general act on the prevention of pollution. In section 7 of the act is the soil pollution prohibition. The use of Best Available Technology (BAT) is written as a legal principle in section 4 of EPA, and it applies to all activities within the scope of the act. The regulation of contaminated soil was removed from the Waste Act (1072/1993) to the new Environmental Protection Act, in which chapter 12 is titled "Treatment of polluted soil and groundwater."

A decree on the *assessment of the decree of pollution and the need for restoration* of the soil is currently being prepared in the ministry of the environment.

B. Waste Legislation

The Waste Act (1072/1993) and Waste Decree (1390/1993) implemented the provisions of Council Directive (75/442/EEC) on waste and Council Directive (91/689/EEC) on hazardous waste. The other European Community provisions on waste and waste management have been implemented through general regulations issued by the Government or the Ministry of the Environment, such as the decree on the incineration of hazardous waste (842/1997)etc.

The definitions of waste and hazardous waste in the Finnish Waste Act is similar to the definitions in the Waste Framework Directive 875/442/EEC and Council Directive (91/689/EEC) on hazardous waste. Therefore polluted soil material is always classified as waste. Whether polluted soil is hazardous waste, is decided on case by case basis. The decree on landfills implements the Council Directive on Landfills (99/31/EC). Polluted soil is within the scope of the decree. So, even special landfills for polluted soil have to meet all the legal demands of the landfill decree.

The Waste Tax Act (495/1996 changed by 1157/1998) lays a tax on all waste disposed on municipal landfills. However, polluted soil is excluded from the scope of the tax.

C. EIA-Legislation

There is a special act (468/1994) and a decree (268/1999) on Environmental Impact Assessment.

2. PERMITS FOR SOIL TREATMENT INSTALLATIONS

A. Procedure for "On Site" Soil Restoration

According to the special rule in the Environmental Protection Act section 78 an environmental permit is required for the treatment of polluted extractable land resources. Action may, however, be initiated to restore soil or to remove polluted soil material for treatment elsewhere by making the relevant notification to the regional environment center if;

- the extent of the polluted soil and the degree of pollution have been adequately established
- treatment observes an approved treatment method in general use; and
- the activity does not result in any other pollution of the environment

The second criterion mentioned above refers to the technique or a method used in the restoration. Apart from removing the soil, restoration methods can be divided into soil washing, stabilization, biopiling, incineration and different soil venting methods. Whatever kind the method is, it has to be familiar in Finland to be subject to notification procedure only. Some prior practice of the method in Finland should be required. Therefore new methods may at first be subject to permit procedure.

The notification is a cheaper and less time consuming procedure compared to permit procedure. In practice a notification is always given first and it is then up to the permit authority to award whether it is sufficient or whether a permit procedure should take place. The permit procedure is according to the legislation a primary rule, and it can be replaced by the notification procedure only if the criteria in the section 78.2 are met. However, in practice more than 90% of the restoration activities since 1.3.2000 have been subject to the notification procedure only.

B. Liability to Apply for a Permit for “Off Site” Treatment of Soil

An environmental permit is required for “institutional or commercial recovery or disposal of waste” (section 28.3). Polluted soil material which has been removed from the soil is considered as waste and therefore falls within the scope of Waste Act and other regulation concerning waste. An “off site” treatment of soil material is considered as recovery or disposal of waste and therefore subject to environmental permit procedure.

There are some derogations concerning the permit requirement in section 28 of the Environmental Protection Act. Small scale recovery or disposal activities neither institutional nor commercial) can be excused from the permit requirement. In addition, permit is not required for “short-term activities undertaken on a trial basis when the purpose is to test a raw material for fuel, manufacturing or incineration method or treatment equipment, or to investigate the impact, usefulness or other corresponding feature of such activities.” In these cases a notification according to section 61 of Environmental Protection Act shall be made to the competent permit authority, at least 30 days before starting the activity.

C. Permit Authorities

The regional environment centers (13) issue permits for soil restoration. However, this power can be transferred to a local authority if “special causes” exist (section 80). In practice the transfer of power is possible only to big municipalities which can offer the expertise needed. The application of transferring the power is handled by the ministry of the environment. So far only Helsinki municipality environment centre has been transferred the power of handling notifications (not issuing permits) according to section 78 in Environmental Protection Act. No other municipality has applied for transfer of powers.

Following rules according to the Environmental Protection Decree sections 6-7 apply when polluted soil material is restored “off site” (waste disposal or recovery): The regional environment centers (13) issue permits for restoration in which the minimum capacity is 5000 tons of waste per year. The municipality issues permits for smaller activities.

D. Summary of the Permit Procedures Concerning Soil Restoration

Soil restoration activities are in the first place permitted according to the special procedures stated in section 78 (permit or notification). In most cases only a *notification to the regional environment centre* (in Helsinki the municipal environment centre) is required. According to section 28, a permit is required for the “off site” treatment as well (recovery or disposal of waste). However, if the soil material is restored or treated “on site”, only the procedure in section 78 applies.

Table 1: Summary of possible procedures concerning restoration of polluted soil.

Legal basis	When?	Derogations?	Competent authority
EPA 78 § (permit or notification)	always for restoration (on site)	No	regional environment centre (In Helsinki municipal env. centre)
EPA 28.2 § (permit)	when the soil material is removed and taken "off site" for treatment	short-term testing of method, equipment or impact (EPA 30 §) → notification	regional environment centre or municipal authority

In general, the new procedure according to section 78 in the Environmental Protection Act is considered to be fluent. Testing of new clean-up techniques is possible by using the notification procedure according to sections 30 and 61 in the Environmental Protection Act. Presentation of new techniques in factual restoration projects, however, should at first be subject to the permit procedure according to section 78.

For mobile establishments (which have recently been introduced in soil restoration) some problems may arise, when the restoration of the soil material (waste) has to be done "off site" - this might be because of the technique exceeds the emission limits for a certain area. "Off site" treatment of the soil is subject to permit procedure according to section 28 in the Environmental Protection Act and cab not be done inside the procedure according to section 78 in the act.

Location of the activity is one of the legal considerations for granting the permit. So, mobile activities as such can not be permitted since the exact location of the activity can not be defined. Instead, small mobile technologies/plants are treated the same as large capacity immovable soil treatment plants; a separate environmental permit is needed for every site where the treatment activity takes place.

3. ENVIRONMENTAL IMPACT ASSESSSMENT (EIA)

A. Restoration of Soil

According to the general rule in the Act on Environmental Impact Assessment (468/1994) section 4, EIA applies to all activities which "may cause significant impacts to the environment." Most of such activities are listed in the decree on EIA (268/1999). However, if the activity is not listed in the decree, the general rule mentioned above may still apply. The restoration of soil may become subject to EIA if it "may cause significant impacts to the environment." However, the ruling interpretation in Finland is that soil restoration is not subject to EIA since restoration as such endeavors on cleaning the environment, not polluting. EIA could only become relevant in severe restoration projects in which there would be a potential danger of harmful impacts to soil or groundwater.

B. Recovery or Disposal of Soil Material (Waste)

"Institutional or commercial recovery or disposal of waste" (section 28.3) may become subject to EIA on the basis of criteria set out in the EIA-decree section 6. An "off site" disposal or recovery of polluted soil material can become subject to EIA. In considering whether or not EIA applies, relevance is given to the *amount of waste*, the *classification of the waste* and the *technology* at issue.

In case of *physical or chemical* purification or *incineration* of the soil material, the minimum capacity of 5000 tons per year is the limit for EIA if the soil material is classified as *hazardous waste*. If the soil material is classified as *(ordinary) waste*, the minimum capacity of activities/establishments subject to EIA is 100 tons per day. *Biological treatment* of waste is subject to EIA if the capacity of the plant/establishment is 20 000 tons per year at the minimum. In case of d*isposal*, more than 50 000 tons of waste per year is always subject to EIA.

C. Summary of Applying EIA in Soil Restoration

A soil restoration project is, according to the ruling interpretation of the law among authorities, not subject to EIA. However, soil cleaning plants in cases where the soil is removed from the soil, can be subject to EIA if the conditions in the EIA-decree section 6 are met. If the soil is classified as hazardous waste, EIA is required for relatively small capacity plants/establishments. Biopiling is considered as a biological treatment of waste and therefore subject to EIA if the capacity of the establishment is 20 00 tons per year or more.

For mobile soil treatment plants/technologies, a similar problem in relation to EIA exist as in relation to environmental permit: EIA is by definition a location based instrument and therefore the EIA requirement should be assessed case by case on all different “off site” treatment/restoration locations.

4. SUBSTANTIVE LAW CONCERNING SOIL RESTORATION

Recognition of a polluted soil is found in EPA section 7: “…deterioration of soil quality as may endanger or harm health or environment, may substantially impair the amenity of the site or cause comparable violation of the public or private good.” The definition is broad and no consistent practice has bee developed, although some unofficial guidance (a memorandum of the ministry of the environment 1994) has been available about target-values and limit-values of different harmful substances in the soil. However, a new decree on *assessment of the decree of pollution and the need for restoration.* The new decree will introduce the criteria for soil pollution (target-values, limit-values) and the need for restoration.

5. USE OF TREATED SOIL MATERIALS

There is no special legislation or other criteria concerning the use of contaminated soil in earthworks. Guidelines (non-legal) on reuse have been prepared in Finnish Environment Institute. Until now treated soil waste has been reused for construction of landfills and earthworks of industrial and storage areas as other wastes also.

6. CLASSIFICATION OF THE SOIL AND ITS LEGAL EFFECTS

Classification of polluted soil as waste or hazardous waste has been a controversial issue and interpretations in different regional authorities have been inconsistent. In many cases the classification has been based on the proposed interim limit values of contaminated soil. Due to this, a major part of the removed soil material has been classified as hazardous waste. According to new criteria most of the soil removed from contaminated sites shall not be classified as hazardous waste.

Despite the renewed criteria, some of the removed soil will still be classified as hazardous waste. The classification of the soil as *hazardous waste* has at least the following relevant legal effects:

1. EIA applies for all plants/establishments with a capacity of at least 5000 tons per year.
2. In the case of incineration techniques, the *decree on hazardous waste incineration (842/1997)* is applied. This decree regulates the technical standards and especially the emissions to air. In practice, hazardous waste incineration is not allowed on delicate areas, such as housing or recreation areas.
3. For removing the soil “off site”, a certain transport document is issued.
4. If a permit is required for recovery or disposal of waste (section 28 in EPA), a financial guarantee is required to cover the possible malfunctions in the activity.
5. The disposal or recovery on hazardous waste can not be released from permit requirement. (For a non hazardous waste treatment plant a derogation from the permit requirement is possible according to the EPA section 30. This possibility is originally based on the Waste Framework Directive art. 11)

7. SUMMARY

In general, the *material regulation* in Finland concerning environmental technology, emissions to soil, water and air does not hamper the implementation of new remediation technologies. On the contrary, the principle of Best Available Technology is a general principle in the Environmental Protection Act (section 4), and it applies to all activities. The waste legislation at present in most cases allows the treatment of polluted soil without applying the regulation concerning hazardous waste – this should encourage the presentation of new methods and technologies.

The *procedural regulation* of restoring contaminated sites is also considered to be quite fluent by all. In most cases, only a notification to the competent authority is needed. However, the environmental permit system may in some cases hamper the use or introduction of new technologies. Especially removable soil treatment plants, which in most cases are both environmentally and economically feasible, may become subject to a double permit procedure. This is however only in cases, where the removed soil material has to be taken "off site" for treatment; permit may be required for both the restoration project and the treatment of the soil material.

The economic burden on the disposal of polluted soil does not in every possible way support the treatment of polluted soil. Even though polluted soil is subject to landfill regulation and the indirect economic burden there off, the disposal of polluted soil is still excluded from the scope of waste tax.

8. THE SOIL TREATMENT MARKET IN FINLAND

In recent years about 200 polluted sites have been restored per year. A sum of approx. 30-35 million euros is used every year in restoring. During the next 10-15 years, at the minimum 3000 sites should be restored, at the cost of approx. 0,4-0,8 billion euros. Closed mines or the treatment of removed water sediments is not included in these calculations. In total 20 000 sites in Finland have been classified as "potentially contaminated." About 10 companies which the Finnish market on soil remediation. Also some new companies are intending to enter the market – both from Finland and other countries. Some new technologies have even been introduced, such as bioremediation techniques, reactive barrier solutions, electrokinetic methods and phytoremediation.

In addition there are 54 (1998) permitted locations where it is possible to compost soils contaminated by oil based compounds and case by case also other substances which are verified to be compostable.

There are 5-7 consultant enterprises which offer case by case services to manage contaminated sites combining different technologies.

FRANCE

1. LEGAL AND ADMINISTRATIVE ISSUES

A. Background Information on Legal and Legislative Action

It may be considered that the French policy in matter of polluted land has been defined in its general features and objectives by the December 3rd 1996 circular letter of the Minister of the Environment. This policy can be characterized by a will of efficiency and realism. The circular letter includes a paragraph entitled: "*The principles of a realistic policy for the treatment of polluted sites and soils*", in which it is written that "*...it is a long term action, to the scale of the century and half of industrial history of our country. The development of this policy can only be progressive and according to the public and private means that will be possible to mobilize...*".

Another aspect of this policy is the principle of dialogue, also mentioned in the circular letter of December 1993. This principle is put in practice between the Ministry of the Environment and the different actors that take part in the management of polluted sites: governmental agencies (ADEME, Water Agencies), industrial operators of potentially polluting installations, associations for the protection of the environment, experts, consultants and enterprises specialized in evaluation and treatment of polluted land and, in the case of pollution related to domestic waste, Municipalities and Territorial Institutions. This dialogue occurs in many occasions, specially in the national working groups that discuss the projects of methodological guides prepared by the Ministry of the Environment, before these guides are issued as references for technical regulations.

B. Summary of Legislation

In the case of polluted sites, the basic legal reference is the **law of July 19, 1976** on the Installations Registered for the Purpose of Environmental Protection (*Installations Classées pour la Protection de l'Environnement*: IC Law), which covers all environmental aspects of industrial activities (including waste management and treatment or disposal). According to this law industrial installations have to be either authorized (if they have potentially a strong environmental impact) or declared (if they have potentially a little environmental impact). Another basic reference, which may be applied in the case of pollution of land, is the **law of July 15, 1975** on elimination of waste and recovery materials (*Elimination des Déchets et Récupération des Matériaux: Wa*ste Law). Additional laws, improving the management of the environment, complete the I.C. and waste laws:

- **Law of July 13th 1992** created a new policy for the management of domestic wastes including:
    - the progressive banishment of direct landfilling of waste within a time limit of ten years,
    - the institution of a tax on the direct landfilling of domestic waste,
    - **a specific section on the selling of industrial land, where installations regulated by the IC Law have been operated, that oblige the vendor to inform the purchaser of the possibility of the pollution of the considered land. In this situation the purchaser has the possibility to cancel or to renegotiate the sale**.

- **Law of February 2nd 1995** regulated the procedures in the case of "orphan" polluted sites and finance this action by the extension of the waste tax (law of July 1992) to special (polluting) industrial waste treated or disposed in collective installations.

- **Law of Dec. 31 1998 (finance law)** that creates a new general tax on polluting activities (TGAP). This tax replaces different previously existing taxes and is applied on air pollution, noise, used oils, treatment / disposal of domestic and industrial waste.

In connection to these laws, additional legislative decrees and circular letters (directives) have been issued, mainly:

- **decree of September 21, 1977**, that defines the obligations of the operator of an industrial installation in the case of cessation of activity
- **circular letter of December 3, 1993**, defining the policy for polluted sites
- **circular letters of April. 3 and 18, 1996**, requiring the realization of preliminary diagnostic and simplified risk assessment for active industrial sites
- **circular letter of June 7, 1996**, describing the procedure to be carried out to apply the polluter pays principle.
- **circular letter of Sept. 1, 1997**, indicating the possibilities to imply the owner of the polluted site.
- **circular letter of March 11, 1999**, specifying administrative and legal procedures applicable to polluted sites remediation
- **circular letter of December 10, 1999***,* listing the principals to fix the remedial objectives

C. The Concept of Polluted Sites

At the origin in 1978 and during the eighties, problems of polluted sites and soils were systematically related with problems of wastes.

A wider concept of pollution of land designated by "polluted sites and soils" was introduced at the beginning of the nineties. Accordingly, on December 3, 1993, the circular letter dealing with the "policy of rehabilitation and treatment of polluted sites and soils" was issued by the Minister of the Environment and gathered the main elements of a new policy for the subject encompassing:

- a systematic registration of potentially polluted sites
- a concerted definition of priorities
- the treatment of every polluted site according to its impact and the use of the land.

At the present time, the definition of a polluted site is: ***site generating a risk, either actual or potential, for human health or the environment related to the pollution of one of the medias, resulting of past or present activities***.

Practically, polluted sites are industrial sites, active or inactive, waste sites, and accidental pollution sites.

D. Administrative Aspects

Although there is a recent tendency towards some regionalization, France remains a centralized country. For the environment, like for other subjects, laws are discussed and voted by the parliament and regulations are enacted by the Government and have a national validity. At the central level, the Ministry of the Environment is responsible for the management of the environmental policy. More precisely, inside the Ministry of the Environment, the Department in charge of industrial pollution and waste management, including the problem of polluted sites is the Direction of Prevention of Pollution and Risks (*Direction de la Prévention des Pollutions et des Risques*: DPPR). At the local level the basic geographical administrative unit is the "***departement***" (there are 99 ***departements*** in the country), and in every department, the Prefect, who is the representative of the government, is responsible for the implementation of the regulations. In the particular case of polluted sites, for which, the basic framework law is the Law on Registered Installations (IC Law, mentioned above in b). The Prefect is assisted by the Inspectors of the Registered Installations who control industrial activities (including waste management and disposal) and who are in almost all cases members of the Regional Direction of Industry, Research and Environment (*Direction Régionale de l'Industrie, de la Recherche et de l'Environnement*: DRIRE).

Basically the legal and administrative action is based on the polluter pays principle, the polluter being, according to the IC Law, the operator of the installation at the origin of the pollution.

The circular letter of the Minister of the Environment of June 7, 1996 gives a detailed definition of the procedure to be carried out by the authorities to manage the suspected or proven contaminated sites according to the polluter pays principle and, in case of unsuccess, to deal with the orphan sites. This procedure may be explained as follows: in the case a registered installation is suspected to be responsible of land pollution, the Prefect may require the operator, according to the IC Law (section 23), to carry out the actions (investigations or clean up) requested by the Inspectorate of Registered Installations (*Inspection des Installations Classées*). If the operator doesn't comply with the order, the Inspector of the Registered Installations writes to the Prefect a report assessing this non execution. In this situation, the Prefect may require the operator to deposit to a public accountant a sum representing the estimated cost of the requested work. If this procedure does not succeed, most of time because of insolvency of the operator, the public accountant states the insolvency of the responsible party to the Prefect who will then send the file of the considered case to the Ministry of the Environment, requiring the site to be considered as "orphan". If the Ministry agrees, the case is presented to the specific National Commission of the Agency of the Environment and Energy Management (ADEME) to be financed by public funding (TGAP). Then, if the case is accepted by the Committee, the Prefect is allowed to issue an order asking ADEME to carry out the requested investigations or clean up. After the requested actions have been carried out ADEME has to initiate lawsuits against potential responsible parties in order to try to get the reimbursement of the public money spent for the case.

The position of the authorities concerning the owner of a polluted site is a subject of active discussion. Some years ago, the position of the Ministry of the environment was rather to consider the owner as a responsible of second row and generally no action was initiated against him. Now this position has changed and the Ministry may require the prefect (circular letter of Sseptember 1, 1997), in the case of failure of the action against the operator of the installation, to engage administrative action against the owner. However the existing jurisprudence is rather controversial and the legal validity new position of the Ministry is not proven.

E. Summary of Policy Developments

As it has been explained above the French approach to deal with polluted sites is basically connected with the legislation on the environmental management of industrial installations (IC Law) and to a more limited degree to the management of waste (waste law).

This means that there is no specific legislation relative to soil protection or polluted sites. Although the development of such legislation has been already considered, it seems that it will probably not happen in the short or middle term and that the existing approach will continue.

In this view the existing laws (IC Law) will be applied and completed by technical directives (circular letters) issued by the Ministry of the Environment to organise the management of polluted sites. These technical directives are related to technical guides developed at the present time.

A first technical guide has been issued in 1996 (draft 0) and 2000 (draft 2) to organise the preliminary evaluation and priority ranking of suspected polluted sites. The proposed preliminary evaluation includes two steps:

Step A: which is a documentary study (a historical review and a vulnerability study) based on available and accessible data, and is completed with a site visit. The historical review includes a description of the sequences of activities that have taken place in the course of time, their precise locations and any associated environmental practices that may have been carried out. The vulnerability study includes an investigation of the parameters (geology, etc.) that could have relevance for the fate and transport of the contaminants and the potential targets (housing, drinking water supply etc.) likely to be affected.

During the site visit the data deriving from the documentation study should be verified and additional data acquired. An evaluation and identification of existing and potential impacts takes place and a further investigation programme is prepared.

Step B: initial diagnosis (and the simplified risk assessment (SRA) includes the collection of data that have not been available within the previous study but are conditional for the simplified risk assessment. The SRA demands an understanding of the contamination's spatial distribution and transport mechanisms, the identification of possible hazards and the description of possible rehabilitation methods. At this stage it is necessary to develop some field investigation in order to acquire the data that make this understanding possible.

Simplified Risk Assessment (SRA); based on the results of the preliminary evaluation, a simplified risk assessment is conducted according to a scoring system: the site in question is classified in one of 3 groups:

- sites needing further investigation and detailed risk assessment
- sites for which monitoring systems should be applied
- sites that can be used for specific purposes without further investigations or implementation of measures

The decision making process within the SRA is supported by defined guideline values.

For the sites where the preliminary diagnostic concludes that the pollution and risks are serious, the realization of the impact study and risk assessment will give the basis to determine the rehabilitation objectives and to select the remedial options.

A second methodological guide, under the responsibility of the Ministry of the Environment, in cooperation with a national working group, has been issued in 2000 (draft 0). This guide defines the objectives and contents of the impact study (detailed investigations) and detailed risk assessment. The risk assessment takes into account the present and future uses of the site and its surrounding, especially for the water and air dispersion routes. Targets taken into account are human health, water resources, ecosystems and buildings. The maximum tolerable excess lifetime cancer risk to be used for defining remedial objectives is 10^{-5}.

The proposed detailed evaluation includes two steps (B Sauvale, D.Darmandrail in *Risk Assessment for Contaminated Sites in Europe-Policy Framework, CARACAS 1999:*

Step A: in-depth diagnosis. The main objectives are:
- to verify or refute hypotheses made following the initial diagnosis, and, in particular, to identify and characterise all sources of pollution and to establish the actual condition of the site.
- to estimate the extent of pollution in the transfer media (this should be done for all media concerned
- to understand the transfer mechanisms of pollutants in these media
- to evaluate (if necessary) the impacts, whether direct, indirect or cumulative
- to collect all the informations needed to implement the detailed risk assessment

Step B: detailed risk assessment which should enable:
- the identification of significant unacceptable risks to human health and other receptors, and which therefore require treatment to reduce or eliminate these risks
- the definition of remedial objectives on the basis of current scientific knowledge, consistent

with the defined land use of a site and its surroundings. These objectives or tolerable risks levels should be both technically and economically realistic
- the determination of a remedial strategy adapted to the site, indicating actions which will enable risks to be reduce

2. REGISTRATION OF CONTAMINATED SITES

Although France was probably one of the first countries to carry out some kind of inventory of polluted sites in 1978, limited attention has been given to the problems of land pollution until the beginning of the nineties.

National register

At the national level, since 1993, a national register is managed by the Ministry of the Environment (DPPR). In this register are gathered the sites that are known by the local authorities and can be considered as polluted.

These sites are listed in a computerized databank (BASOL) and reports are periodically issued by the Ministry to inform the public of the situation. A publication of this register was issued in December 1994, gathering 669 sites; another one based on the situation of December 1996 was issued in December 1997, with 896 polluted sites plus 125 sites already restored without any limitation of use. In June 2001, 3058 polluted sites were inventoried. In February 2002, **3345 polluted sites** were inventoried, including:

- **243** treated sites without use restriction
- **1228** treated sites with use restriction
- **467** industrial sites still working with a programmed simplified risk assessment
- **1407** sites at the present time in evaluation or in remedial operation

Inventories

In addition to this registration system are actions of inventory carried out through two specific ways:

a) The historical inventories, initiated at the regional level (BASIAS data base), based of the consideration of local industrial history in order to discover, in connection with the existence of past polluting industrial activities, the places where pollution can be suspected. These inventories are mainly based on the consideration of the archives and indicate suspected sites (or potentially polluted sites). At the present time (March 2002) such inventories are finished in **33/99** departments (**52 000 sites** have been studied). It is expected that about 200 000 to 300 000 suspected locations will be collected at the end of these studies (2005) for the whole national territory among which some thousands will require corrective action.

b) The evaluation of the pollution of active industrial sites (including industrial waste treatment and disposal sites)
In April 1996, the Ministry of the Environment instructed the Prefects of departments to order the owners of registered installations to carry out preliminary investigations and simplified risk assessment of their sites. A preliminary classification of priority activities to consider in the orders is given in the annexe of the circular letter. Within five years (end 2002) it is previewed that some 2000 sites assigned with priority 1 will be evaluated.

Estimation of the number of polluted sites

The two previously mentioned actions, historical inventories and evaluation of active industrial sites, are not enough developed to allow a significant evaluation. The only very approximative estimation possible at the present time is **200 000 to 300 000 suspected sites** and some thousands of cases requiring corrective actions.

3. REMEDIAL METHODS

A. Summary Data on Remedial Technologies Used in the Country

According to a 2001 study (BIPE, Polluted sites market in France, Confidential), the techniques used for the polluted soils in 400 sites where a rehabilitation project has been carried out can be listed as follows:

- Landfilling: 5-10%
- On site isolation: 10-15%
- In/on site treatment: 20-30%
- Biotreatment (biopiles): 25-30%
- Incineration: 5-10%
- Thermal desorption: 8-10%
- Other: 5-10%

In more than on third of these cases, combination of techniques has been used.

B. Policy Initiative and Other Factors Influencing the Use of Remedial Methods

For the first cases of rehabilitation during the eighties and in the beginning of the nineties, most of the techniques used were isolation and treatment or disposal in the installations of the waste system.

It appeared soon that waste treatment plants (incineration) were often technically inappropriate and very expensive and, because of recent regulations, inducing restrictions of use and technical constraints, landfilling has become more and more difficult and costly.

These circumstances create a positive evolution for the use of specific soil treatment techniques.

C. Methods Used for Remediation

The techniques that have been and are still the most frequently used to clean soils are microbiological degradation and soil venting, but in cases where no treatment technique can be technically or economically applied, isolation remains one of the most frequently used technique,.

Biodegradation is most of the time carried out on site by the mean of composting or bio-piles (**11 biopiles in 2001**). Contaminants degraded are petroleum compounds, light and heavy oils and even polyaromatic hydrocarbons. Soil venting addresses volatiles hydrocarbons and chlorinated solvents in the unsaturated zone. It is sometimes associated with in situ biodegradation (bio-venting). To depollute the satured levels (groundwater) venting is combined with air sparging.

More recently, new treatment capabilities have been made available either by specific own development or by technology transfer. The techniques concerned are soil washing (**solvent washing: one plant in 2001**) and thermal desorption.

At the present time **six thermal treatment installations**, with various level of performance (quantity and complexity of pollution that can be treated) have been made available in France.

4. RESEARCH DEVELOPMENT AND DEMONSTRATION

A. Summary of Government Supported R&D

The support of R & D by the Government is mainly provided by the Ministry of the Environment and the Ministry of Research and Education through three different ways:

- Ministry of the Environment, Section in charge of Research (D4E) that develops research programs focusing on behaviour of contaminants in regard of risks and possibilities of treatment
- Ministry of the Environment, Section in charge of Industrial Environment (SEI) that develops the methodological guidance documents to be used in connection with regulations
- Agency for the Environment and Energy Management (ADEME) in charge of evaluation and rehabilitation of orphans polluted sites that develops specific research programs to improve the basis of decision making procedures and to optimise the choice of remedial techniques and the control of their efficiency.

The total amount of funds made available through these three actions is about **3 M€/year.**

Concerning the development of rehabilitation techniques, some public money is supplied by the Ministries of Research and of Industry through funds to help technical innovation (RITEAU projects) and international cooperation (EUREKA projects).

In addition to governmental funding, some supports to R & D projects are also provided by Regions most of the time in connection with the economical redevelopment of brownfields (North or Lorraine Regions).

B. Private R&D Programs

In addition to research programs financed by public funds, some enterprises develop specific R & D activities (1.5 M€ in 2001). These enterprises can be gathered into two categories:

- Enterprises responsible of polluted sites that are looking for optimisation (technical and economical) of the management of these sites: a typical example of such enterprises is Gaz de France that is in charge of about 467 gaswork sites
- Enterprises that are active in evaluation and/or clean up of polluted sites and that try to improve their know how.

C. Perspectives

According the present time it may be estimated that the R & D programs will be mainly oriented in two directions:

- increase the efficiency of the management of the suspected and proven polluted sites by the preparation of technical guidance documents associated with the development of specific tools to improve the decision making procedures
- develop more economical and efficient equipments and processes to characterise and to treat the pollution.

Considering the treatment techniques, two possibilities are simultaneously developed:

- improvement of existing techniques: a typical example is bioremediation with many projects trying to extend its application to recalcitrant pollutants (PAH, PCB...)
- development of new treatment techniques: reactive walls, supercritical extraction, electro migration...

GERMANY

1. LEGAL AND ADMINISTRATIVE ISSUES

Soil protection and the management of contaminated sites in Germany have been regulated on the federal level since 1999. The Federal Soil Protection Act was enacted on March 1st, the accompanying Soil Protection Ordinance on July 19th.

The act and the ordinance cover most of the items connected with the management of contaminated sites with two major exceptions, where the Laender may provide legal regulations:

- **Identification** (Article 11):
  The Länder may issue provisions regarding identification of contaminated sites and of sites suspected of being contaminated.

- **Experts and Investigating Bodies** (Article 18):
  Experts and investigating bodies that carry out tasks pursuant to this Act shall possess the necessary expert knowledge and reliability for such tasks and shall have the appropriate required equipment. The *Länder* may set forth the details of the requirements pertaining to experts and investigating agencies pursuant to the first sentence of this paragraph, as well as to the nature and extent of their tasks, submission of the results of their activities and the official naming of experts that fulfil the requirements pursuant to the first sentence of this paragraph.

Identification and Registration

The Laender identify and register the sites, which are contaminated, and the sites, which are suspected to be contaminated, according to their own criteria.
The Federal Soil Protection Ordinance gives some hints to be considered:

> (Sites) ... where pollutants were handled ... over an extended period of time or in significant amounts and where operation, management ... or disturbances of proper operation suggest the existence of significant inputs of such substances into the soil. At abandoned waste deposits, such evidence shall in particular be deemed to exist in cases in which the type of operation or the time of closure suggest that the waste was not properly treated, stored or deposited.

The actual inventory shows more than 360.000 registered sites.

Federal States	**Number of (Suspected)**		
	Former Waste Disposal Sites	**Former Industrial Sites**	**Sites**
[1]	[2]	[3]	[4]
Baden-Württemberg	6.229	11.567	17.796
Bavaria	10.034	3.295	13.329
Berlin	763	6.220	6.983
Brandenburg	8.189	14.447	25.313 *
Bremen	173	18.154	18.327
Hamburg	491	1.638	2.129
Hesse	6.630	63.539	70.169
Mecklenburg W.-Pomerania	4.078	7.264	11.342
Lower Saxony	8.957	50.000	58.957
North Rhine-Westphalia	18.116	17.147	35.263

Rhineland-Palatinate	10.578	No Data	10.578
Saarland	1.686	3.530	5.216
Saxony	8.590	19.115	27.705
Saxony-Anhalt	6.296	14.692	20.988
Schleswig-Holstein	3.181	16.451	19.632
Thuringia	6.138	12.824	18.962
Germany Total	**100.129**	**259.883**	**362.689**

Remarks:

- Rhineland-Palatinate will update the inventory in 2001.
- The difference between [4] and the sum of [2] and [3] is due to regional classification.

The Laender are aware of the problem that different criteria will cause different and not comparable data. A first step has now been made to compile the regional criteria for the registration such as:

- Are sites with different reasons for suspicion (for example: former industrial site plus uncontrolled waste disposal) are counted once or twice?
- Are overlapping sites counted once or more than once?
- Will information be deleted about sites which are not anymore suspected to be contaminated?
- Are the inventories based on individual hints or on general estimations?
- Is the process of identification seen as finished?
- Are sites, which have been remediated according to the present use of the site, removed from the registers?

2. REQUIREMENTS PERTAINING TO EXPERTS AND INVESTIGATING AGENCIES

On the behalf of the Committee “Contaminated Sites“ (part of the working group of the Federal Government and the Federal States on “soil protection”) a group of experts worked out regulations concerning the investigation of (suspected) contaminated sites; Title: Guidelines for quality assurance in the field of contaminated sites (Arbeitshilfen zur Qualitätssicherung in der Altlastenbehandlung). Chapters:

- Investigation strategy
- Sampling of soil, air (in the ground) and groundwater
- Treatment of the samples
- Field analysis
- Chemical and biological analysis
- Interpretation and assessment of the results
- Simulation of groundwater flow and transport processes

The Committee has recommended publishing these guidelines for using and testing. The guidelines (until now only German version available) can be downloaded at http://www.lua.nrw.de/altlast/altqs.htm.

3. RESEARCH AND DEVELOPMENT

A. Stars

A Database on about 1,100 relevant environmental substances has been set up by the Federal Environmental Agency with:

1. physical and chemical characteristics of the substances,
2. behavior in the environment (stability, degradation etc.),
3. ecological toxicology (human, mammal, acceptable daily intake),
4. substance specific regulations,industrial health and safety requirements,
6. regulations according of the German soil protection act,
7. regulations of the Federal States.

B. Joint Research Projects

The technology development program is mainly funded by the Federal Ministry for Education and Research (BMBF). There are currently three major projects:

- Treatment Walls for the Remediation of Contaminated Sites
- reliable data for planning and construction
- demonstration of tue environmental impacts
- technological aspects of installation and operation
- (Enhanced) Natural Attenuation
- Prognosis of Leachate from Contaminated Materials

GREECE

1. LEGAL AND ADMINISTRATIVE ISSUES

In Greece the Environmental Law 1650/86 was enacted in 1986 and was designed to cover all aspects of environmental protection. In that law specific provisions were included regarding soil protection from the disposal of municipal and industrial wastes, and from excessive use of fertilisers and pesticides. Although no specific legislation guidelines or standards exist for soil quality, there are several components in Greek law, which refer directly or indirectly to control of soil and groundwater contamination.

Apart from Law 1650/86, the basic elements of Greek legislation related to contaminated sites are two Joint Ministerial Decisions (JMD) dealing with the management of municipal and hazardous wastes respectively. The Municipal Waste Management Act (J.M.D 69728/824/96) was enacted in May 1996 and imposes obligations on local authorities for developing waste management plans. One important issue is the registration of old waste dumps and their gradual elimination through reclamation and rehabilitation. The Hazardous Waste Management Act (JMD 19396/1546/1997) was enacted in July 1997. This Act defines hazardous wastes and refers amongst others, to the duties of the producer or holder of hazardous wastes to avoid contamination of land from hazardous wastes disposal.

In the “National Plan and the Framework of technical specifications, regarding hazardous waste management”, which are being prepared today, a more specific approach to the investigation and management of sites, contaminated by hazardous waste dumping, will be included.

2. CONTAMINATED SITES

The paucity of heavy industry and other production activities that give rise to hazardous wastes has restricted the number of contaminated sites in Greece. Such sites are more likely to be related to improper dumping of household and industrial wastes, to mining spoil and tailings ponds, to petroleum refining and storage sites. So far there has been no specific survey for the identification and registration of contaminated sites in Greece. According to the first inventory of household waste disposal sites in 1988, some 3500 sites were operating without any environmental protection measures, and about 1500 sites with limited measures.

Research carried out by universities and research institutes has identified a number of industrially contaminated sites, including the Lavreotiki Peninsula, the large mining area of Northern Eubea, the Thriassion pedion area in the Attica prefecture, the industrial zones of Thessaloniki and Athens (Schimatari-Inofyta) etc. Today a study is being planned by the Ministry of the Environment for the registration of sites suspected of dumping hazardous wastes.

3. REHABILITATION ACTIVITIES - REMEDIAL METHODS

In recent years, there has been considerable interest in rehabilitation activities, mainly concerning municipal waste disposal sites, but also on sites contaminated from industrial and mining activities. Three major rehabilitation projects concerning municipal wastes disposal sites are currently in progress:

1. The site of Schistos, which stopped operating in 1992
2. The landfill site of Ano Liossia (Attica)
3. The landfill site of Tagarades (Thessaloniki)

Regarding full scale projects for the remediation of contaminated soils, available information is very limited. There is however a number of cases, where industrially polluted soils have been remediated, using the following techniques:

1. Excavation and of site landfilling
2. Ex-situ and in-situ bioventing applied for soils contaminated with organic volatile and semi-volatile compounds
3. Soil vapour extraction applied for volatile contaminants
4. Soil washing applied for the case of soils contaminated with acids
5. Soil flushing applied for soils contaminated with acids, metals and organics.

4. RESEARCH DEVELOPMENT AND DEMONSTRATION

There is no specific National R&D programme in the field of Contaminated Land. However, several Greek Universities and Research Organisations are actively involved in the development of innovative soil remediation technologies, such as:

- In situ chemical stabilisation of heavy metal polluted soils
- Removal of heavy metals from contaminated soils by chemical extraction techniques
- Bioremediation of soils contaminated by heavy metals and metalloids
- Remediation of polluted ground waters using permeable reactive barriers

ITALY

1. LEGAL AND ADMINISTRATIVE ISSUES

After the Ministry Decree (DM) of 1989, which started the collection of regional data on contaminated sites, a more comprehensive national legislation relevant to contaminated sites has been enforced at the beginning of 1997 by the adoption of the Waste Act (D. Lg.vo 22/97); this law provides the institutional framework for contaminated sites assessment and management, and establishes the requirements for the development of the technical and administrative procedures relevant to contaminated sites inventory, characterization and assessment, clean-up, safety measures and monitoring (Art.17). These procedures have been set out in technical and more specific administrative guidelines adopted with the Environment Ministry Decree (DM) 471 of October 25th 1999 which is actually the 'implementation decree' of Art.17 of D.Lg.vo 22/97.

Law 426 of December 9th 1998 establishes a first list of 15 sites of national interest within the National Plan for the Clean-up of Contaminated Sites. The Plan is relevant to sites, which, because of their size, complexity and extent of environmental and health risks, are object of direct involvement and funding from the government. These sites altogether cover an inland and off-shore potentially affected area of over 330,000 hectares, more than 1% of the state territory. The Ministry of the Environment together with the ANPA (National Agency for the Protection of the Environment) and with the other competent national and local agencies and institutions, are responsible for approving and issuing permits relevant to site investigation, assessment and remediation projects.

More recently the National Plan has updated the list that includes now 41 sites and a public investment of approximately 500M euros for the years 2001-2003. The budget will be mostly dedicated to cover costs of investigations and emergency safety projects. By a preliminary estimate the overall area potentially affected by the sites of national interest, should cover around 2% of the state territory. The list includes major poles of the oil, chemical, steel works, asbestos and mining industry, partly or entirely dismissed, together with some large areas affected by illegal waste dumping. In some cases projects are carried out according to formal agreements between stakeholders and control bodies.

The sites of national interest add to the regional inventories of contaminated sites, which accounts now for approximately 10,000 sites plus 6,000 gas stations. So far though only four out of 20 regions have completed their inventory and formally approved the remediation plan, with priorities and costs, by regional laws.

The total estimated cost, for long term remediation of national and regional sites amounts to approximately 30,000-35,000M euros.

2. REGISTRATION OF CONTAMINATED SITES

Three different procedures are envisaged by DM 471/99 to register and to initiate actions at contaminated sites:

- a notice that is communicated to local authorities from the polluter;
- an ordinance that is issued by controlling authorities; and
- voluntary registration and actions, on behalf of site owners, especially for historic contamination episodes.

Obligations and schedules for contaminated site notice communication, under procedure 1, to Municipality and Regional authority are established. Tasks and powers of local authorities and competent institutions in issuing ordinances to parties responsible of pollution are defined under procedure 2.

Ordinances are issued by competent Municipality. For procedure 3, that also requires a formal registration of the site to local authorities; the deadline has been established within current year 2001. Public sites and sites lacking of an identified responsible party, are also collected in the register. Regions define priorities of actions on registered sites.

The sequence of actions implemented at contaminated sites is the following:

- definition of site boundaries and owners
- description of main features and prevailing pollution problems
- definition and implementation of emergency actions when needed
- definition and implementation of site characterization plan
- definition of remediation and environmental restoration plan
- planning of safety actions in order to protect site workers and residents
- implementation of health monitoring programs, when needed, in order to track the extent and trend of past exposures
- plan of technical, professional, institutional and occupational requirements
- plan of financial requirements

All projects for investigation and remediation must be approved by the competent local or national authority.

3. REMEDIAL METHODS IN USE

In situ and on site methods are in principle encouraged together with the reuse of off-site treated soils. Solutions that reduce long term control and monitoring needs are privileged.

As a general comment, one and a-half experience with the new legislation has proved a positive stimulation in remediation initiatives; nevertheless, some limitation in the ability to force present site owners to take care of pollution generated by past activities at the same site, is recorded. Furthermore restrictive quality criteria for soil, especially for the case of materials excavated and exported from the polluted site, limit the number of cleanup and reuse options. As a consequence of the new national legislation, regions in the north industrial areas of the country, if on one side are experiencing an increase in actions aimed at restoring contaminated sites, on the other side are recording some percentage increase of containment and soil dumping solutions with respect to practices used under former regional laws.

Several demonstrated and emerging technologies are being applied for cleanup of soil and groundwater. On the basis of a preliminary screening within major engineering companies and most active regions, static and hydraulic containment account for more than 70% of remedial techniques applied. Soil vapor extraction and soil venting, for cleanup of volatiles in the unsaturated zone, play a major role with approximately 40% of techniques sometimes applied jointly with hydraulic containment of contaminated aquifers. Consolidated or innovative on site techniques are also experienced in some cases. Off site technologies are quite limited because of legal restrictions on the exportation, transportation, processing and reuse of polluted soil.

4. RESEARCH AND TECHNOLOGY DEVELOPMENT PROGRAMS

There is no specific national program for technology development. Nevertheless research activities are being carried out by academic and research institutions under sponsorship of the Ministry for Scientific and Technological Research, the Ministry for the Environment, the National Agency for the Environmental Protection, the EU Commission and the national oil industry.

A research and development laboratory has been recently (2001) established at the ACNA industrial contaminated 'site of national interest' as part of its rehabilitation program. The laboratory, mostly funded by the government and under agreement with local authorities, will be managed by an academic consortium for environmental chemistry. Remediation projects with biological and chemical technologies will be carried out by several research units. Following the starting period, the laboratory will become a national "Center of Excellence" for further research and development of remediation technologies and a national reference in this field.

JAPAN

In recent years, there has been a very marked increase in the number of cases of identified soil contamination due to hazardous substances in Japan. Fears of damage to human health have been growing, as have social demands for the establishment of measures against soil contamination. Based on such a situation, in order to ensure the safety and peace of mind of the Japanese citizens, the Soil Pollution Control Bill was approved by the Cabinet on February 15, 2002 and submitted to the 154th ordinary session of the Diet for deliberation. The Soil Pollution Control Bill stipulates the execution of soil investigations to identify and characterize soil contamination and control measures against soil contamination to prevent damage to human health due to soil contamination.

1. BACKGROUND

Once soil is contaminated by hazardous substances, there is the possibility that adverse effects on human health will occur due to direct intake of the contaminated soil or drinking of the groundwater containing the hazardous substances eluted from the contaminated soil. Soil contamination caused by heavy metals and volatile organic compounds has been uncovered with the redevelopment of former factory sites in recent years, although there were few cases of such soil contamination identified heretofore. In particular, the number of cases of identified soil contamination due to hazardous substances has increased remarkably in Japan, and a large number of cases of newly identified types of soil contamination has been reported in the last several years.

Soil contamination by hazardous substances is liable to cause adverse effects on human health if the contamination is left untreated. In order to prevent groundwater pollution and clean up contaminated groundwater, a prohibition against underground infiltration treatment and purification control measures based on the Water Pollution Control Law have been taken; however, there are no laws regarding control measures against soil pollution in Japan. The fears of damage to human health have increased, and the social demands for the establishment of measures against soil contamination have been strengthened. Based on this situation, the Ministry of Environment organized the “Committee for Institutionalization of Soil Pollution Control,” which consists of economists, legal scholars, citizens, representatives from industry, chemists, toxicologists and environmental engineers, in December 2000. The Committee subsequently examined and considered the institutionalization of various soil pollution control measures and summarized their findings in an interim report in September 2001. In response to the interim report, the Minister of Environment asked the Central Environmental Council to develop a system for future soil environmental protection measures in October 2001. The Central Environmental Council established a subcommittee for deliberation into this matter. The subcommittee held six hearings on a future system for soil environmental protection measures, and its final report was issued on January 25, 2002 through a public comment procedure. The Ministry of Environment drafted the Soil Pollution Control Bill on the basis of the final report and submitted it to the current ordinary session of the Diet.

2. OBJECTIVES

In order to protect the health of citizens, the soil pollution control measures, which stipulate investigations to identify and characterize soil contamination and control measures to prevent damage to human health due to soil contamination, should be implemented. The basic aims of the soil pollution control measures are the control of the dispersion of the soil contamination that has already occurred as well as the control of the occurrence of new soil contamination caused by the discharge of pollutants.

To date, a number of measures have already been taken by the Japanese government. As a control measure to prevent the occurrence of new soil contamination by the discharge of pollutants, the prohibition against underground infiltration treatment of effluents containing hazardous substances and the regulation of effluents by effluent standards set for factories based on the Water Pollution Control Law have been taken. Water purification control measures are also prescribed by the Water Pollution Control Law. In addition, regulatory measures for the appropriate treatment of waste are prescribed by the

Waste Disposal and Public Cleansing Law, and regulations against soot and smoke emission from factories are mandated by the Air Pollution Control Law. Furthermore, the Law Concerning Special Measures against Dioxins regulates the emission of dioxins.

Hence to some extent it is believed that institutionalization of regulatory measures has already been done for the control of the new occurrence of soil contamination that originates from the emission of the pollutants associated with the production activities described above. However, sufficient institutionalization has not been carried out for the control of the dispersion of the soil contamination that has already occurred. Therefore, it is believed that institutionalizing regulations establishing the responsibility and procedures for the soil surveys and measures regarding the soil contamination that has already occurred will prevent the dispersion of soil contamination. The following sections provide an outline of the contents of the proposed bill.

3. INVESTIGATION OF SOIL CONTAMINATION

The landowners shall have the responsibility of carrying out the soil examinations because they hold the title to the land and the rights to make changes in the land like the digging that needs to be done to perform the surveys, and they also have the responsibility for the condition of the land. The landowners should perform surveys of land that has the possibility of soil contamination due to the reasons given below. Here, landowners are defined as the existing landowner, occupying person (e.g. tenant) or manager (e.g. bankruptcy receiver).

- **Examination of land that was the site of a factory, including a specified facility where operations were halted by law (the Water Pollution Control Law defines a specified facility as one where hazardous substances are produced, used, or treated)**: The landowner of land that was the former site of a factory, including any specified facility where operations were prohibited, shall request the surveying organization designated by the Minister of Environment to investigate possible contamination of the land in question, and report the results to the governor of the prefecture. (Any land that the governor of the prefecture recognizes as having no possibility of causing damage to human health in terms of land use is eliminated as an object of survey).

- **Examination of land where there is the possibility that damage to human health may happen due to soil contamination**: When the governor of a prefecture deems that the land has the possibility of causing human health damage due to soil contamination, he may require the landowner of the land in question to ask the designated survey organization to examine the land for soil contamination and to report the results.

4. DESIGNATION OF CONTAMINATED LAND AND PREPARATION OF LEDGER OF DESIGNATED AREAS

In case of the land not being in compliance with soil environmental standards, the governor of a prefecture shall officially designate the area as such and publicly declare the contaminated area of the land as the designated area. Prefectural governors shall prepare ledgers of the designated areas, and anyone may inspect these ledgers.

5. PREVENTION MEASURES AGAINST DAMAGE TO HUMAN HEALTH BY SOIL CONTAMINATION

A. Contamination Removal and Clean-up Measures

Should the actual polluter be the target of the prevention measures against soil contamination, the following problems may arise. First, the polluter may have no title to the contaminated land and thus be unable to implement the preventive measures. Second, there is the risk that the soil contamination may be left as it is if it is impossible to identify the actual polluter of the soil or if the polluter no longer exists. On the other hand, the landowner has the responsibility for land that is dangerous to human health due to contamination. Furthermore, the landowner has the title to the land and can thus make changes in the land like the digging that needs to be done to clean up the contaminated soil; the landowner has the overall responsibility about the condition of the land. Should the governor of the prefecture deem that the land has the possibility of causing damage to human health due to soil contamination inside a designated area, he may order the landowner of the land in question to remove and clean-up the soil contamination.

The bill stipulates that the governor of a prefecture may order the polluter to remove and clean up the contamination in cases where the polluter is identified easily and the landowner agrees to make the polluter take necessary clean-up measures. Here, the regulation governing the removal and clean-up of contamination includes restricting entrance to the area by putting up signs prohibiting entry, laying top soil cover and pavement to prevent direct ingestion of contaminated soil, and containing and cleaning up groundwater pathways leading from the contaminated soil. The basic idea is that the environmental risk associated with soil contamination should be reduced by blocking the exposure to pathways that may cause adverse effects on human health due to soil contamination.

B. Request for Payment of Costs Incurred for the Removal and Clean-up of Contaminated Soil

Should the landowner need to take measures for the removal and clean-up of contaminated soil in response to the above-mentioned order from the prefectural governor, the landowner may request the polluter to bear the cost required for the removal and clean-up operation.

C. Notification of Change in Form and Quality of the Land and Order for Making Changes in the Alteration Plan

The parties who try to change the characteristic form and quality of the land inside the designated area shall be required to notify the governor of the prefecture of their intention and plan to do so. The governor of the prefecture may order the notifying parties to make alterations in the execution plan for changing the characteristic form and quality of the land should he deem that the execution method does not comply with the technical standards set by regulations.

6. DESIGNATED SURVEY ORGANIZATION

The Minister of Environment shall designate as authorized survey organizations those survey and analysis companies having appropriate technical ability in order to ensure the reliability of soil contamination surveys.

LATVIA

The information in this tour de table is current as of January 2002.

The Republic of Latvia has a huge amount of old contaminated sites inherited from the former Soviet System. The largest portion of these sites consists of former Soviet military sites, many of which need remediation activities. This makes the situation very specific as it is impossible to use the principle "polluter pays," which step by step starts to be the main principle in a solution of current environmental problems in Latvia. There the polluter is well known but it will never pay, especially if it is former Soviet Army. It means that it is necessary to look for specific ways to solve this problem. This creates huge economical and juridical difficulties. From one side, the State does not have resources to pay for clean up activities. From other side, most landowners, which received their properties in the processes of denationalization and privatization, also do not have enough resources. They also ask for rules for dealing with pollution on their lands, which is polluted by others in previous times; but such rules are still not defined. A similar situation exists with international investors who are interested to run their business in some former military sites, such as naval bases, airfields, different reparation plans etc. This means that at present moment, the polluted former military sites are not only an environmental problem, but a hindrance to the growth of economics as it creates difficulties for investments. This is also a huge problem for the Latvian Armed Forces as our military units mainly are stationed in former Russian military bases.

The goals of the ongoing and past activities in an area of polluted sites are to:

- create economic and juridical mechanisms for solution of the historical pollution problem;
- implement the principle "polluter pays" for current activities; and
- form economic and juridical mechanisms for pollution prevention and pollution control.

Site remediation predominantly will take place as part of the normal commercial redevelopment of land with funding considered at the level of individual site and not as part of specific overall national environmental improvement program. An inception could be the sites with a very high level of risk to human health and environment. Therefore the most urgent task is to set up a legislative base for contaminated sites and pollution prevention. Currently, the "Law on Pollution" is adopted by the Cabinet of Ministers of the Republic of Latvia and has been in force since July 2001.

The purpose of this law is to prevent and reduce damage on human health, property, and the environment caused by pollution, to counteract consequences of such damage and to:

- prevent pollution or, where that is not possible, to reduce emissions to air, water and soil arising from polluting activities;
- prevent or, where that is not possible, to reduce the use of non-renewable natural resources and energy at polluting activities;
- prevent or, where that is not possible, to minimise the generation of waste;
- provide for inventory and registration of contaminated and potentially contaminated areas lying within the national territory;
- determine the measures for investigation of contaminated and potentially contaminated areas and for remediation of contaminated areas;
- identify the persons, who shall cover the investigation costs of contaminated and potentially contaminated areas and the remediation costs of contaminated areas.

This law determines the requirements on the operator concerning pollution prevention and control and a procedure for pollution prevention and control, including, *inter alia*:

- requirements for start-up, operation and cessation of polluting activities;
- permitting conditions for polluting activities and water use, and a notification procedure for those

polluting activities, which are not subject to authorisation;
- a procedure for laying down environmental quality standards;
- a procedure for laying down emission limit values for certain substances, conditions on polluting activities and other restrictions on the operation of polluting activities;
- a procedure for inventory, registration, investigation, and remediation of contaminated areas;
- conditions on supervision, control and monitoring of polluting activities and a public information procedure.

This law applies also to certain mobile sources, identified by the Cabinet of Ministers. Activities involving radioactive substances, nuclear waste, sources of ionising radiation, and genetically modified organisms are regulated by other legislation. The Regional Environmental Boards (under the MEPRD) carry out the monitoring and control of polluted territories except the military territories that are under the response of Ministry of Defence.

Unfortunately, at present moment we have little time to see how the law "works". About the effectiveness of the Law of Pollution and obtained experience and results the first presentation could be given at the beginning of the next year.

But now I would like to return to contaminated sites by the Soviet Army. First of all, it is necessary to mention that currently the ecological assessment of former military sites has been done using a single set of methods. This has been done into the framework of Latvian-Norwegian cooperation project. The experts of the Latvian and Norwegian Geological Surveys assessed and investigated more then 600 former Soviet military sites, 255 of which were incorporated in a special computerized database. The database contains all information collected during the studies of former military sites.

The Latvian and Norwegian specialists developed criteria, based on which all sites have been subdivided into four groups:

1st group – it is evident that site is polluted with hazardous substances and poisons that spread into the environment or the site is contaminated with explosives that all together could cause essential threat to human life and to the environment, detailed investigations and clean-up activities are urgent;

2nd group – there is only some information about pollution of the site with hazardous substances that could cause threat to human life and to the environment. Further site investigations are required.

3rd group – pollution of site is insignificant and the possibility of migration of hazardous substances also is insignificant. Site investigations are required only in case of change of land use;

4th group – no evidence of pollution and hazardous materials. Further site investigations are not required.

According to the mentioned criteria 255 main former military sites were assessed and result was following:

1st group – 14 sites:
2nd group – 17 sites;
3rd group – 62 sites;
4th group – 171 sites.

The most dangerous for human health and the environment is 1st group that consists of 7 former rocket bases, 2 big fuel stations, 1 very large bombing range, 1 ammunition storage site, 1 airfield, 1 tank reparation plant, and 1 submarine base in former Liepaja Naval Base.

Petroleum pollution of the soil was found to be the most widespread of all the problems resulting from the Soviet Army's activities. The most polluted petroleum areas were found in places where fuel and lubricants were pumped, stored, and transported as well as in the sites where transport and combat materials were washed (especially after accidental spills). Almost in all detailed investigated fuel storage sites free phase oil has been found.

Unexploded ordnance in former bombing ranges and ammunition storage sites (especially if explosives are deep in soil) is another very serious problem.

Detailed pollution investigations are carried out only at some of military sites, and have mainly been done with assistance of our donor countries (Denmark, Norway, Germany, and Canada as well as the USA and Sweden).

Up until now, clean-up activities have been carried out only in some of the most harmful sites. Mainly, those are pilot projects with the purpose of finding the best clean-up technologies and preventing the spread of hazardous substances to drinking water reservoirs and ambient surface water bodies.

The Latvian Ministry of Defense and the Ministry of Environmental Protection and Regional development have incorporated environmentally sound approaches in practice of military training. In these undertakings, very important support is being received on a USA and Swedish initiated project – so named the Environmental security project. The main purpose of this project is to:

- strengthen the cooperation and coordination between military and civilian organizations; and
- train military personnel in environmental management to prevent further degradation.

In the framework of this project, the Latvian, U.S., and Swedish military and environment officials agreed to cooperate to develop the Environmental Base management Plan for Adazi Military Training Base. The management plan served as a pilot project, and during the project period they:

- established objectives and developed procedures to achieve sound environmental management;
- determined the level of environmental training necessary for personnel at various stages of command;
- set priorities and monitored clean-up activities that must take place in order to ensure the continued operations of the base; and
- initiated activities aimed at preventing further environmental damage or pollution, wastewater treatment, hazardous waste management, land management for control of erosion and protection of rare and endangered species.

Also I would like to mention Liepaja Naval Base Project. Liepaja was the biggest Soviet Navy Base in the Baltic Sea. Now this former base is being transformed into a commercial port. The Special Economic Zone is established in the territory of former base.

From the beginning, the Liepaja project was a part of Phase 2 of the NATO/CCMS Pilot Study on Environmental aspects of Reusing Former Military Lands. Recently, the project was transformed into partnership project between Canadian public-private sector consortium, the City Council of Liepaja, Liepaja Special Economic Zone and the Latvian Government to share information on managing the redevelopment of large former military sites. The Canadian side the project was financed by the Canadian International Development agency.

The main objective of this project is was to work out the comprehensive strategy for the long-term cleanup and marketing of the Navy Base District. The main approaches used in the Republic of Latvia for solution of the problem of contaminated sites are to:

- use a co-financing approach for funding necessary investigation and clean-up activities (state, municipality, international donor, and private means),
- make assessment of pollution (common and in some cases also very detailed) of former military sites,
- organize training for Latvian specialists (including military personnel),

- get as much assistance as possible from international organizations and from bilateral cooperation with main donor countries,
- carry out some clean-up pilot projects at the most significant harmful sites, and
- negotiate with landowners, investors etc. in every concrete case about terms of clean-up activities (clean-up standards, budgeting, land tax reductions etc.

LITHUANIA

The information in this tour de table is current as of January 2001.

1. INTRODUCTION

The Republic of Lithuania is a small country on the Baltic Sea. It occupies an area of 65.600 km, with a population of 3.7 million, or 56 people per sq. km. The five largest Lithuanian cities are:

- Vilnius (600,000 people),
- Kaunas (400,000 people),
- Klaipeda (200,000 people),
- Šiauliai (150,000 people), and
- Panevežys (130,000 people).

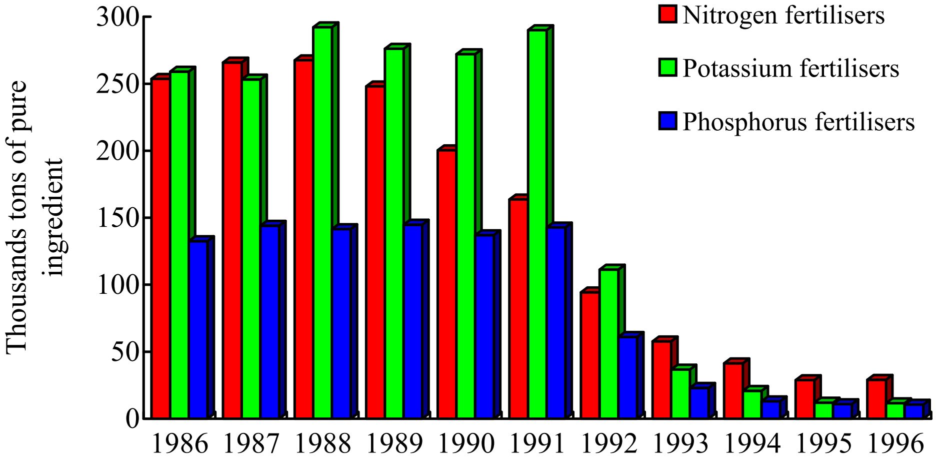
These cities are the largest industrial centres and, at the same time, the main polluters of soil and groundwater. Along with these industrial centres, Mazeikiai Oil Refinery, Akmene Cement Plant, Jonava and Kedainiai Fertiliser Plants, as well as road and railway transport and agricultural enterprises are among most significant polluters. Many contaminated sites were left in former Soviet military bases. In rural settlements, there are territories contaminated with agrochemicals, oil products, or simply waste.

2. SOIL CONTAMINATION AND ECONOMY

It should be noted that the extent of pollution caused by industry and agriculture has decreased considerably since 1990, because after the fall of the Soviet Empire, unilateral economic links orientated towards the East were disrupted. This exerted a negative effect upon the development of Lithuanian economy. Today the government of the Republic of Lithuania, businessmen, and industrialists attempt to develop economic links in all directions, with Western countries in particular. However, this process is difficult, and it will take much time until Lithuanian economy has recovered. The volume of production has decreased several times. Therefore current soil, water, and air pollution levels are considerably lower.

The current poor economic condition of Lithuanian industry and agriculture is clearly good for reducing the risk of soil pollution. Decreased level of diffuse soil pollution from agriculture is a good example of the current situation. The amount of fertilisers and pesticides used in agriculture is now about 10 times less as compared with the figures of 1986-1989 (see Figure 1 and 2). Farmers and communities are still buying some mineral fertilisers, but the majority is limiting use to minimum application rates.

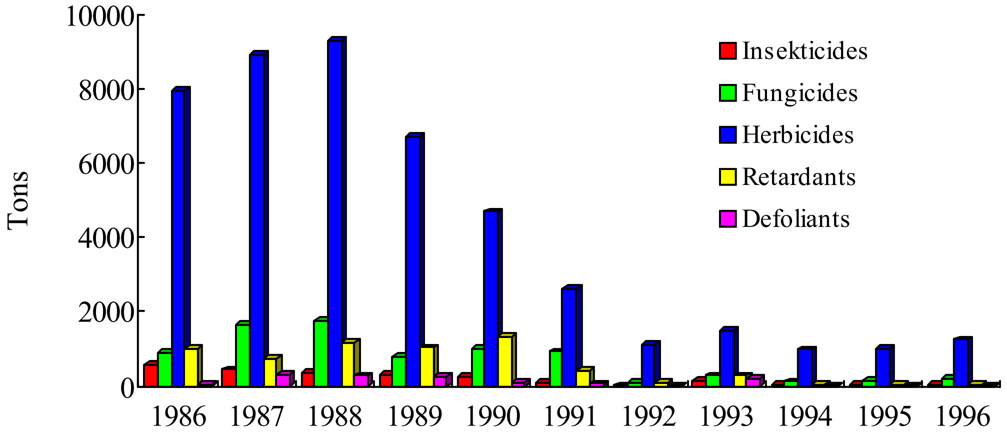
Figure 1: Total Usage of Nitrogen, Phosphorus and Potassium Fertilisers in Lithuania (1986-1996)



Following the re-establishment of independence in Lithuania and the collapse of the collective farm system, levels of production and the use of pesticides decreased significantly. Currently only the most profitable farms are making extensive use of pesticides since these are the only enterprises that can afford both the spray products and good (often reconditioned) spraying equipment. Nonetheless the rates of pesticide application remain limited by high price so there is a tendency towards economic and rational use. This is particularly so with herbicides since manual labour is very cheap and hand-weeding of crops is very common.

Average pesticide use is less than 2 kg active ingredient per hectare which is very low compared to some EU Member States (e.g., The Netherlands) and much lower than levels of use during the Soviet period. However, the use of pesticides is now gradually increasing again, notably herbicides (Figure 2).

Figure 2: Total Usage of Various Pesticides in Lithuania



Current situation: More rationale application, more effective storage, handling, spraying etc., mainly due to rather high prices of agrochemicals, resulted not only in decreased diffuse soil pollution, but also reduced the probability of cases when soils are contaminated heavily. Earlier quite often it was resulted by poor storage and handling of unused agrochemicals (especially pesticides) much of which was stored in leaking containers or else discarded in the forest or village dump.

Of course the improving economic situation will result in increase of mineral fertiliser and pesticide application. The same tendency could be traced in industry.

3. INFORMATION ABOUT CONTAMINATED SITES

Information about contaminated sites in Lithuania is not very exhaustive. The best situation concerns contaminated sites in former Soviet military bases. A detailed investigation was carried according to the project "Inventory of Damage and Cost Estimate of the Remediation of Former Military Sites in Lithuania" financed by the PHARE Programme of the European Community. The Project was completed at the beginning of 1995. The results achieved are useful for the Ministry of Environmental Protection when planning future remediation activities. During the investigation, 275 Military bases of the former Soviet Union were registered. They occupied more than 1% of the country's territory. As the survey shows, the number of military units located in Lithuania totaled 421. The size of Military bases greatly varies - from less than 100 m^2 (a workshop) to almost 14 000 ha (forestry). Judging by the number of pollution and environmental damage cases registered in the military bases (see Table 1), pollution with oil products (21% of military bases) and wastes (17% of military bases) prevail, alongside with the damage to landscape and soil (16% and 29%, respectively). Soil pollution with heavy metals, rocket propellant, cases of radioactivity also were stated.

Table 1: Number of Pollution and Environmental Damage Cases Registered in the Territories of Former Military Bases

Type of the environmental damage	Number of cases	Total territory (ha)	Distribution according to the damage type (%)
Oil products	566	399	20
Mechanical soil damage	778	11137	29
Damage to landscape	438	7140	16
Wastes	478	1288	17
Damage to forest	249	3293	9
Bacteriological/biological pollution	137	14	5
Hazardous chemicals	56	p/p*	2
Radioactivity	9	p/p	0,2
Rocket propellant	20	p/p	1
Explosives	12	p/p	1

*p/p - point-source pollution

Having analysed the results of the inventory performed at military areas, 10 bases were selected for a detailed investigation. Geological-hydrological and environment pollution investigations were conducted on a broad scale. The results of the investigations were submitted in 25 volumes in Lithuanian and English. It was also calculated that cleaning of the contaminated military sites to the permitted contamination levels requires huge funds–about 730 million USD.

Many contaminated sites connected with transport and transport accidents - including roadsides polluted by road and railway transport, bus/railway station, petrol pump territories, etc. Many polluted territories are situated near Klaipeda (the Lithuanian port), through which up to 10 million tons of oil and oil products are carried every year. The territory of Oil Terminal Company in Klaipeda is considerably polluted. There are more than 110,000 cubic meters of soil and ground with oil levels reaching 10 000 ppm.

Another dangerous source–storage places, dumps of old pesticides and other agrochemicals. In the 954 storages of the country, about 2,200 tons of pesticides that are unsuitable and prohibited from using are accumulated. These pesticides must be immediately utilised because cases of fire are frequent in such storages. There are large quantities of contaminated ground in the territories of these storages. Investigation and cleaning of these territories also requires considerable investment.

An inventory of Lithuanian landfills and other waste territories was also carried out in 1994. No comprehensive information still concerning industrial contaminated sites

Cleaning of contaminated ground to a larger extent has been started in Lithuania just in 1995. The largest soil bioremediation site is located near the city of Klaipeda. Costs for remediation of 1 m^3 of contaminated soil is about 60-70 USD. Potential polluters (plants, enterprises, agrocompanies, etc.) are forced to carry out investigations of pollution parameters (composition, concentration, total area, migration to groundwater) and, if necessary, to plan soil remediation and utilisation activities. Mainly ex situ bioremediation or civil engineering based methods (excavation/disposal, dilution) are used. Phytoremediation is also being applied. Practically no innovative chemical or physical process based techniques are being used in Lithuania, mainly because of high treatment costs.

4. STRATEGY AND POLICIES

Although the main environmental priorities in Lithuania have been assigned to water and atmosphere protection, at present more and more attention is given to soil protection issues. One of the priorities included into Lithuanian Environmental Strategy (approved in the Parliament on 25 September 1996) is soil quality improvement and sufficient formation of land use structure.

In Environmental Status Review of the Strategy, it has been stated that soil and upper ground layer is most heavily contaminated in cities, especially in industrial areas, near highways, fly-overs and also in former military areas. The main goals for soil protection from pollution are as follows:

- reduction of soil pollution rising from use of manure, artificial fertilisers and other agricultural chemicals (plant protection products);
- reduction of soil pollution with oil products;
- reduction of soil pollution with heavy metals (especially in cities and industrial areas)

Besides, soil protection issues have been included in such environmental protection sector as reduction of ground water pollution.

In the Action Programme of the Strategy, the following activities concerning soil pollution have been indicated:

- preparation of Draft Soil Protection Law;
- preparation of soil quality and monitoring standards and norms;
- implementation of environmental sound means of fertilising and use of plant protection products;
- preparation of Draft Law on Liability for Past Environmental Damage (legislation for management of contaminated sites renaturalisation);
- compilation of inventory of polluted areas, including the former Soviet military sites, and development of cleanup and renaturalisation programmes;
- creation of polluted sites data base and monitoring plans.

The main activity concerning soil protection included in Action Program of the Strategy is the Draft Soil Protection Law. This draft was prepared and presented to Government in July 1998. Following obligations for land (soil) users has been stated in the draft law:

- to take care of soil fertility;
- to take care of fertile layer of the soil while carrying-out earthworks (such as construction, building, exploitation of mineral resources quarries, etc.) and use this layer for damaged soil recultivation;
- to implement preservative measures for soil erosion prevention;
- to use manure, artificial fertilisers and plant protection products strictly according established requirements;
- to prevent pollution of soil with waste, waste waters, radioactive, biological, poisoning and other substances harmful for human health and environment;
- to present all obligatory information on soil quality and use conditions for control institutions;
- to inform control institutions in case of soil pollution (accidental spills) and to take measures for cleanup of soil and stop migration of pollutants to other environmental components (ground and surface water, etc.).

Draft Soil Protection Law is prepared like framework, and corresponding regulations, rules and recommendations are necessary for its implementation (some of them are already in force or under preparation). The Parliament of Lithuania decided to include provisions of Draft Soil Protection Law into the Law on Land but until now such decision is not implemented.

Another important document concerning contaminated sites is Lithuanian Waste Management Law (has come into force since 1 July, 1998). A new Lithuanian Waste Management Strategy is also being discussed.

Other normative documents concerning soil and ground quality are:

1. Hazardous Substances: Maximum Permitted and Temporary Permitted Concentrations in Soil. Hygiene Norm - HN 60-1996.
2. Recommendations for Evaluation of Soil Chemical Contamination, 1997.
3. The Maximum Permitted Level of Oil Products in the Upper Lithosphere (Ground) Layer - LAND (Lithuanian Environmental Normative Document) 12-1996.
4. The Regulations of Sewage Sludge Application, LAND 20-1996.

Standards, defining soil quality, sampling procedures, sewage sludge application on land (on the basis of LAND 20-1996) are in the nearest future plans. All the above-mentioned Lithuanian environmental documents are expected to be fully harmonised with EU regulations, directives and standards.

5. CONCLUSIONS

There is lack of comprehensive information about contaminated industrial sites. Inventory studies also should be done of such potential sources of soil pollution as oil tanks, pesticide, fertiliser storages, sewage sludge filtration fields, territories of previous accidents related with hazardous substances, etc. As a rule soil and even ground water around such territories is heavily contaminated. The Lithuanian Geological Survey prepared a database and started an inventory of contaminated areas and potential point sources of contamination. Because of Lithuania’s poor economy, soil remediation activities are not financed on state scale. No innovative process based techniques are being applied in Lithuania, mainly because of high treatment costs.

THE NETHERLANDS

The information in this tour de table is current as of January 2002.

1. LEGAL AND ADMINISTRATIVE ISSUES

The Netherlands policy on contaminated land has been focused on the restoration to multifunctionality up to 1998. The application of the multifunctionality approach to the estimated 110,000 seriously contaminated sites would have incurred costs of around € 50 billion. The Netherlands is now spending about € 0.5 billion per annum, which equals the sum that was initially thought to be sufficient to resolve the entire problem. But at this speed it would take about 100 years to end the operation.

In the meantime soil contamination would hamper construction and redevelopment essential to economic and social development, and dispersal of contaminants in the groundwater keeps on making the problem even bigger. For this reason another policy has been introduced. This policy development is known by its acronym BEVER.

The new approach abandons the strict requirement for contamination to be removed to the maximum extent, and instead permits clean-up on the basis of suitability for use. At the same time government proposed other changes to soil protection legislation, including greater devolution of responsibility for clean-up to local authorities and the creation of more stimulating instruments.

Basically the policy has switched from a sectoral to an integrated approach. This means that the market has to play a more prominent role and take more of the financial burden.
Soil contamination should not only be treated as an environmental problem. The soil contamination policy should also be geared to other social activities such as spatial planning and social and economic development and vice versa.

The strategy is:

- to protect clean soil
- to optimise use of contaminated soil
- to improve the quality of contaminated soil where necessary
- to monitor soil quality

This new approach will be paired to stimulation of the development and application of new technology and to a more cost-effective organisation of the actual clean-up. These measures taken together are expected to cut costs by 30-50%.

In this approach remediation is part of a comprehensive policy regarding soil contamination. Prevention, land use, treatment of excavated soil, reuse of excavated soil (for example as building material), monitoring of soil quality and remediation have to be geared to each other in a more sophisticated manner. This “internal” integration is being promoted under the concept of “active” soil management.

To stimulate market investment a different approach to government funding is announced. The taxpayers’ money will be used in such a way that it evokes private investment. This will be done by improving the existing financial instruments and by the creation of a private sector contaminated land fund. The legal instruments will be made more effective.

The discretion of provinces and municipalities will be further enlarged to create the flexibility, which is needed to initiate and stimulate the measures that are best suited to the local situation (tailor made solutions).

With these measures Dutch government wants to achieve ambitious objects:

- Within 25 years all sites should be made suitable for use and further dispersal stopped. That means that each year almost four times as much sites will have to be remediated as is the case now.
- Presuming that the costs will be reduced with 30-50%, this requires a duplication of the total annual expenditure on soil remediation.
- In order to monitor the results of these efforts and to make information on soil quality accessible to the general public (for example potential buyers) and to authorities (for example planning authorities) we want to have a system of soil quality maps covering the whole country in 2005.

In 1999 a lot of attention is paid to the introduction and implementation of the new approach.

2. REGISTRATION OF CONTAMINATED SITES

Based on the Soil Protection Act there are two driving forces to investigate soil quality:

- Anyone intending to excavate and to move soil for building activities, has to report the quality of the soil to provincial authorities;
- Companies who don’t want to investigate the soil quality on a voluntary basis might be obliged to do so.

Based on these activities a lot of seriously contaminated sites have been identified. These numbers have increased enormously since the first case at Lekkerkerk.

Table 1: Inventory of sites

Year	Seriously contaminated sites	Estimated costs (€)
1980	350	0.5 billion
1986	1,600	3 billion
1999	110,000	15-25 billion*

* based on new policy

3. REMEDIAL METHODS

In the new policy the remediation goal is “Function-oriented and cost-effective remediation”. The Cabinet chose this new remediation goal in its standpoint on the renewal of the soil remediation policy of June 1997. The new remediation goal has been worked out in the report, “From funnel to sieve”. Here the summary of this report is mentioned.

Delineation

The new remediation goal applies to serious soil contamination caused before 1987.
The new goal does not affect the need for remediation and the time at which it must take place. For the decision-making on 'need' and 'time' the intervention values and the urgency system remain unaltered in effect. Finally, the new remediation goal only applies to contaminated terrestrial soils, not to aquatic sediments.

Strategy

The starting-point in the new Consideration Process for the remediation goal is an *integral* approach to the *whole* case of soil contamination. The approach differs for the top soil and the subsoil. In the approach to the top soil, a difference is made according to the type of soil use. The prevention of contact with the contamination is all-important. In the approach to the subsoil it is a question of removing contaminating substances. In this connection, the costs also determine the result to be achieved. The end result must lead to as limited as possible care about residual contamination. At calibration times the remediator checks whether the desired remediation result is being obtained.

Routes

There are three routes for obtaining an approved remediation plan:

- via a standard approach per case or cluster of cases. By this means the decision-making may be simpler;
- via custom-made work per case or cluster of cases. This is obvious if the standard approach offers no solutions.
- via custom-made work per area. This variant is possible in exceptional cases. The remediation goal is tailed to special features of an area.

The motto here is: *'standard approach if possible, custom work if necessary'*.

The Top Soil

In the standard approach for the top soil one produces a living layer. The thickness and the quality of this are dependent on the type of soil use. For two types of soil use soil cultivation values are determined for substances which occur in quantity. These apply as a back remediation value when removing soil and as a quality requirement for soil to be applied. The standard approach results in a limited care scope. In special situations custom work per case is possible with good motives. Determining the remediation goal for the type of soil use, agriculture and nature, is always custom work per case. The authorised authority exceptionally determines a special area result for specific areas. This may be lower or higher than the soil cultivation values. Custom work per area will come about through a democratic procedure.

The Subsoil

The standard approach for the subsoil is aimed at removing contaminating substances to the level of the so-called 'stable end situation'. This level is dependent on the soil structure and the substances present. One must reach the stable end situation per case in 30 years maximum. The starting-point is as complete as removal as possible of the source of contamination, cost-effective removal of the 'plume' and the combating of further spread. In the remediation period one may - under certain circumstances use the soil as a reactor vessel, without source and plume too. Calibration times are built in in order to be able to investigate the extent to which one is on the road towards the stable end situation and to be able to adjust if necessary.

Here too, custom work per case or cluster of cases is possible and - in exceptional cases - custom work per area.

Care

In function-oriented and cost-effective remediation, residual contamination remains in the soil in many cases. Therefore, 'care' is required. This care may consist of:

- registration (establishment)
- monitoring (measuring);
- after-care (active measures).

The burden of the care increases as less far-reaching remediation measures are taken. A firm component of the remediation plan is a care plan. This contains the care measures the remediator takes.

Responsibility

The causer of the pollution or the owner of the location is responsible for the remediation measures and the associated costs.

After the remediation the remediator or the owner remains responsible for carrying out the care measures. If at a location a change to a more sensitive type of soil use takes place whereby extra remediation is necessary, the costs of this are charged to the person initiating the change in the soil use.

Reduction in Costs

The previous Cabinet accepted that with a new consideration method for a remediation goal a savings in costs of 35-50 per cent can be made. We have examined the possible savings in more detail. From this it appears that this assumption was correct. We presume that the cost reduction can be attained as follows:

- approximately 30 per cent by the new standard approach;
- approximately 10 per cent by cleaning and draining off less contaminated groundwater;
- approximately 5 per cent by custom work per area.

Monitoring will show the extent to which the cost reduction will be achieved.

Decision-Taking

The Consideration Process for the new remediation goal is a good opportunity for the proper authority to streamline the assessment of the plans and the execution.

The Law on Environmental Control provides for various methods of granting licences 'in a sly way'. In analogy to this, we suggest surveying the following possibilities:

The proper authority and interested parties will make agreements on the approach to more or less remediation cases. Testing of individual cases on main lines alone thereby becomes possible more easily; making more use of a differentiated system of arrangements whereby types of standard approach and cases of custom work can be assessed in a proper manner.

The effectiveness and the efficiency of the soil remediation operation should thereby be assisted.

Quality

The proper authority must check on quality more so than formerly in all stages of execution. The guarantee of this will therefore become even more important for all the parties involved. The proper authority must also check the quality in the field.

4. RESEARCH, DEVELOPMENT AND DEMONSTRATION

Knowledge is essential for the implementation of policy. In conjunction with the introduction of new policy R&D has been started. R&D on sustainable land management is managed by the Centre for soil quality management and knowledge transfer, SKB. The SKB is dedicated to the quality of the soil from the point of view of controlled risks for man and the environment, without losing track of the financial aspect. In other words, the SKB wants to contribute to more efficient methods for soil remediation and to the development of soil protection and soil management as instruments for preventing (further) soil contamination. The SKB is a co-operative body involving all parties interested in soil management, i.e. trade and industry as well as the authorities. Initially, the activities will be set up for a period of four years (1999-2002), with a possible continuation until 2009.

The mission of SKB is: “To develop and to disseminate knowledge about the functional and cost-effective realisation of a soil quality appropriate to the desired use”. The mission perfectly matches the new Dutch government policy on soil remediation, i.e. functional remediation and cost-effective contaminant removal. (BEVER).

A. R&D Themes

The SKB anticipates initiatives in the following areas of attention:

Urban Development and Restructuring

Integration of the new development and the restructuring of urban centres in combination with the remediation of contaminated locations, such as former (gas) works sites.

Restructuring Natural Areas

Nature development and re-designation of agricultural areas in combination with the remediation of former dump sites and contaminated dredging sludge.

Water Systems Management

Integrating the management of surface water and deep groundwater with the quality of the soil, which consists of earth and groundwater.

Remediation of Existing Contaminated Locations

Developing cost effective remediation strategies and methods for contaminated locations, in which risk assessment, environmental merit, weighing alternatives and in situ methods are important issues.

Maintenance and Soil Management

Risk assessment, management and monitoring of residual (mobile) contaminants will receive increasing attention because it will often be impossible to fully remove the contamination. Moreover, measures will have to be taken to prevent new contamination.

B. Duration of SKB

Initially, the activities will be set up for a period of four years (1999-2002), with a possible continuation until 2009.

C. Budget of SKB

A demand-driven programme also implies the joint financing of the activities by all interested parties. The annual costs of the SKB, estimated at € 6.6 million are therefore borne by the government via an ICES contribution (€ 4.5 million) and by public/private market parties (€ 2 million)]. ICES is an instrument if the government to strengthen the knowledge infrastructure.

5. CONCLUSIONS

The Netherlands policy has been changed drastically in 1997. The introduction and implementation of the new approach is on full swing. In 1999 the new remediation goal, “Function-oriented and cost-effective remediation” has been defined. The basic approach is that the quality of the topsoil should fit in the function of the soil, the subsoil is only remediated if there is a risk by mobile contaminants.
The SKB, a centre for knowledge development and transfer is stimulating the introduction of the new approach and the knowledge development. The SKB started in 1999 and there are now (September 2001) about 80 ongoing projects.

Addresses:

Policy
Ministry of Housing, Spatial Planning and the Environment
Site: www.vrom.nl

R&D
Centre for Soil Quality Management and Knowledge Transfer
E-mail: skb@cur.nl
Site: www.bodembreed.nl

NORWAY

The information in this tour de table is current as of January 2001.

1. LEGAL AND ADMINISTRATIVE ISSUES

The Pollution Control Act from 1981 is the main law regulating clean up of contaminated land in Norway. The polluter pays principle forms an important basis of the Pollution Control Act. If the original polluter can no longer be identified or held responsible, the current land owner may be held liable for investigations and remedial actions.

The Pollution Control Act gives the authorities a very strong legislative tool for clean up of contaminated land. Consequently, industrial companies may be held responsible for historic contamination which occured before they took over the site or on their property before contaminated soil was regulated (i.e., before Pollution Control Act).

Norway has developed a system for risk assessment of contaminated land which is reported in SFT report 99:06 "Guidelines on risk assessment of contaminated sites." Generic criteria related to sensitive land use have been calculated and the model for this is documented in the report. The system involves a step by step approach where alternative and site spesific acceptance criteria can be generated and also allows qualitative methods.

Two simple computer applications are available as excel spread sheet and on the internet at the following addresses: http://www.risiko-forurensetgrunn.ffi.no and http://www.miljoringen.no. This will also be available on SFTs home page http://www.sft.no.

Registration of Contaminated Sites

Contaminated land in Norway is considered as a significant source for contamination of rivers, lakes and fjords. The potential impact from industry, contaminated sediments and landfills on the marine environment is of greatest concern. In some fjords reduced intake of seafood is recommended, due to pollutants such as heavy metals, PCBs, PAHs or dioxins.

The actual status shows that more than 3500 contaminated sites are now registered in Norway. About 2100 of these sites are considered to have a potential for causing environmental problems. About 100 of these have been given high priority and investigations and remediation have been started. Additionally ca. 500 sites need to be investigated. The remaining 1500 sites are considered not to represent environmental problems as long as they remain undisturbed (recent land use). Changed land use or construction work will lead to new assessments for these sites.

The Norwegian government established new national goals for the clean up of contaminated land in October 1999:

- The most seriously contaminated sites shall be cleaned by end of 2005 (about 100 sites).
- Decisions on investigation and clean up on the secondly most contaminated sites by end of 2005 (500 sites).

Investigations and clean up will be carried out and paid for by privat and state owned companies as polluters and responsible parties according to the law.

A GIS database was developed to keep track of all registered sites and any investigation or remedial action carried out at the different sites. This database is now being changed and designed for public use and will be available on internet by the end of next year.

ROMANIA

Romania continues its effort for the transposition of EU legislation in the environmental sector and improves the institutional structures and legal tools.

The main progresses, in the last period of time, September 2001 – May 2002, have been recorded in the legislative and administrative fields.

1. LEGAL AND ADMINISTRATIVE ISSUES

In order to prevent pollution of the environment, the regulatory framework changes continuously and new legislation has been issued.

For law enforcement, The Ecological Guard has been created as a distinct structure of the Ministry of Waters and Environmental Protection. It acts at central and local level.

Some of the most important regulatory acts are listed below:

- Law no. 622/2001 for joining to the European Environmental Agency (EEA) and European Information and Observation of Environment Network (EIONET)
- Law no. 544/2001 regarding the free access to the information of public interest
- Governmental Decision no. 1167/2001 for the establishment of The Environmental Guard
- Governmental Decision no. 96/2002 regarding the endowment of The Ecological Guard
- Governmental Decision 1097/2001 for establishment of Inter-ministerial Committee for coordination of the integration of environmental protection within the sectoral policies and strategies at national level
- Governmental Decision no. 1174/2001 for approval of the organizational structure and functioning of the Administration of the Environmental Fund
- Ministerial Order no. 22740/2001 for approval of the Technical Instructions regarding the supervision of the Compliance Schedule and Environment Recovery Plan by the mining activities
- Governmental Decision no. 118/2002 for approval of the National Action Plan for pollution reduction of the surface and ground waters caused by hazardous substances discharges
- Governmental Decision no. 162/2002 regarding waste storage
- Emergency Ordinance no. 34/2002 regarding prevention, reduction and integrated control of pollution (IPPC)
- Permitting procedure from 2002 for activities having impact on environment
- Ministerial Order no. 116/2002 for approval of the Methodology regarding the assessment of safety of dams and ponds that are storing industrial waste – NTHL-022 and NTHL-023
- Ministerial Order 118/2002 for approval of the Permitting Procedure for Safe Operation of Dams, NTHL-032

The Ministry of Waters and Environmental Protection has developed an extensive Plan for harmonization with the EU legislation included within the National Plan for EU Accession, Chapter 22, Environmental Protection (www.mappm.ro).

2. REGISTRATION OF CONTAMINATED SITES

The National Plan for Waste Management for 2001 has not been published yet. It is to be assumed that it will realize a more complete inventory of the waste deposits and characterize their potential impact on environment.

Comparing to the previous statistics, it is expected that the number of identified contaminated sites will increase.

3. TECHNOLOGY DEVELOPMENT PROGRAM

The National Research Plan, redrawn at the end of 2001, includes more environmental projects that touch rehabilitation technologies.

The National Agency for Mineral Resources and Ministry of Waters and Environmental Protection have issued technical norms for rehabilitation of contaminated sites due to the mining activities.

Ministry of Industry and Resources, Ministry of Waters and Environmental Protection, Ministry of Education and Research and their related research institutes has developed certain programs for rehabilitation technologies.

4. REMEDIAL METHODS IN USE

There are not new remedial methods in use for cleaning up the contaminated soil and ground water. Even so, the most common methods have been applied on a small scale.

Recently, the rehabilitation of soil and groundwater on a larger area starts to be developed on a site affected by tailing storage, close to Baia Mare City. The remedial method that is used consists in a combination of techniques: site isolation, impermeable and reactive permeable barriers.

5. RESEARCH AND DEVELOPMENT ACTIVITIES

The research and development activities continue to be carried out by the existing national institutes for environmental protection and certain universities.

There is not any initiative regarding this field within the private sector.

SLOVENIA

1. INTRODUCTION

At previous Tour de Table presentations I have presented some major Slovenian environmental issues and the legislation that has been adopted in this area. Last year, Slovenia concluded EU negotiations on the environment, and thus closed the environment chapter. Of course, the Ministry of the Environment and Spatial Planning and the parliament continue to draw up and adopt many environment-related implementing regulations but the actual applicative activities related to the protection of the environment are minimal since there is practically no activity in certain sectors.

This presentation aims to explain the issues related to contaminated Karst caves and the recording of industrial waste landfills.

2. BRIEF SERVEY OF WASTE-CONTAMINATED CAVES

Geologically, more than 70 per cent of Slovenia is of karstic character. The Karst world is distinguished by characteristic surface and underground formations created by the chemical effects of water on soluble rock material. Surface formations are mainly hollows; underground formations are mainly karstic caves. These phenomena are a consequence of the rock composition, i.e. calcite (calcium carbonate – $CaCO_3$), which is poorly soluble in pure water. However in water containing dissolved CO_2 with calcium carbonate produces the easily soluble calcium bicarbonate – $Ca(HCO_3)_2$. Because of chemical unbalance, calcite ($CaCO_3$) is often deposited in the form of stalactites and sinter. About 70 per cent of Slovenia is karstic terrain, i.e. Alpine Karst, Karst highlands, Dinaric Karst and pre-Alpine Karst. Figure 1 shows karstic areas in Slovenia.

One consequence of the large extent of karstic features in Slovenia are the karstic caves, whose number is approximately 6,700 according to the register of caves. Some of them are well-known around the world and attract tourists with their stalactites and other karst phenomena. The largest of all is Postojna cave with 19.4 km of tunnels, followed by Križna cave (8.2 km of tunnels), Planina cave (6.1 km of tunnels), Škocjan caves (5 km of tunnels), Vilenica, Tabor cave and Pekel.

In the past, people and industry have used many of the caves, particularly the smaller and the shallower ones, as dumping places for waste of different types. Records show that 694 caves are contaminated with waste of some type. Unfortunately, some of them are still used for dumping waste and some are irreparably damaged or destroyed.

Figure 1: Karst in Slovenia

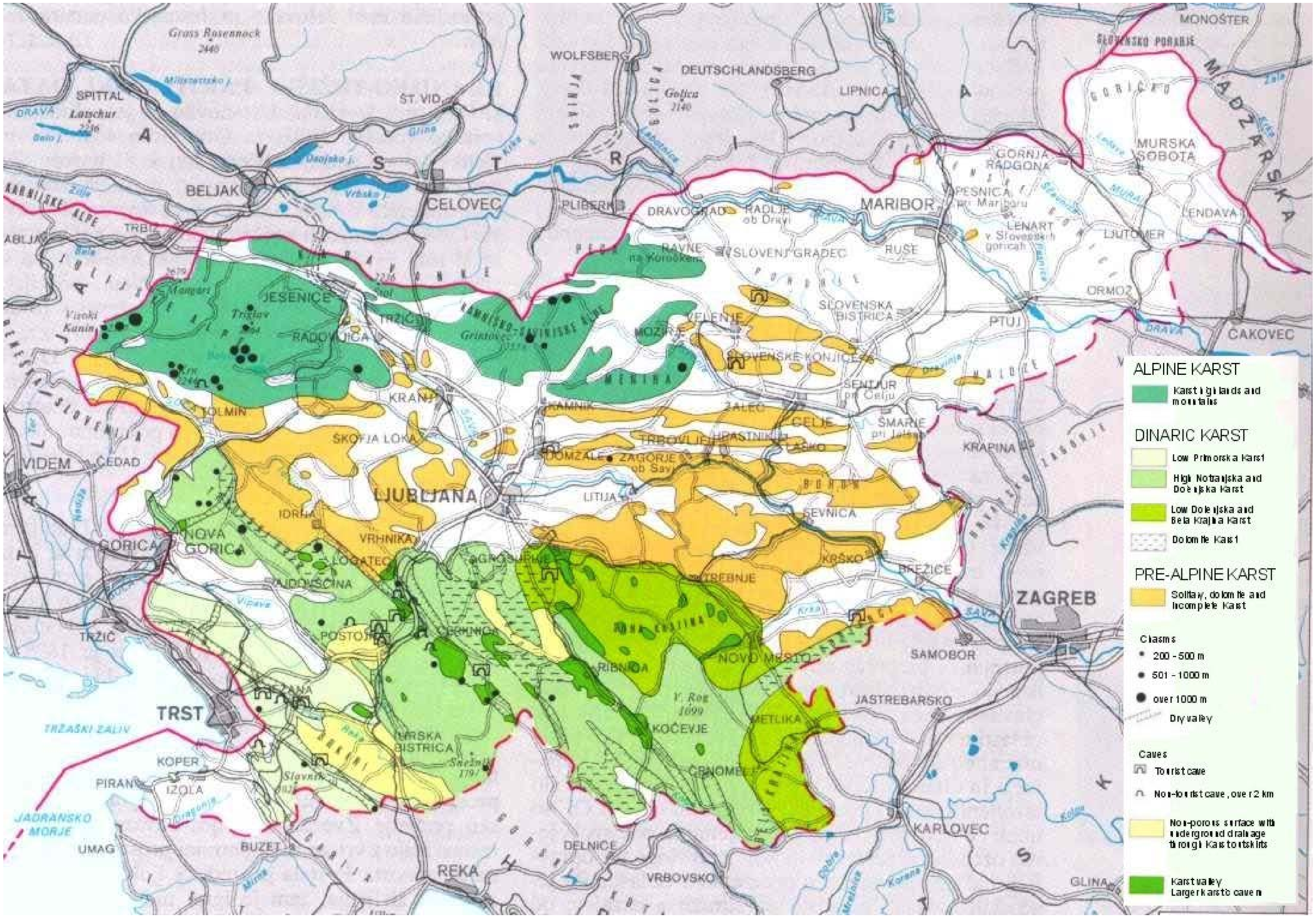


Figure 2: All caves in Slovenia from the register of caves

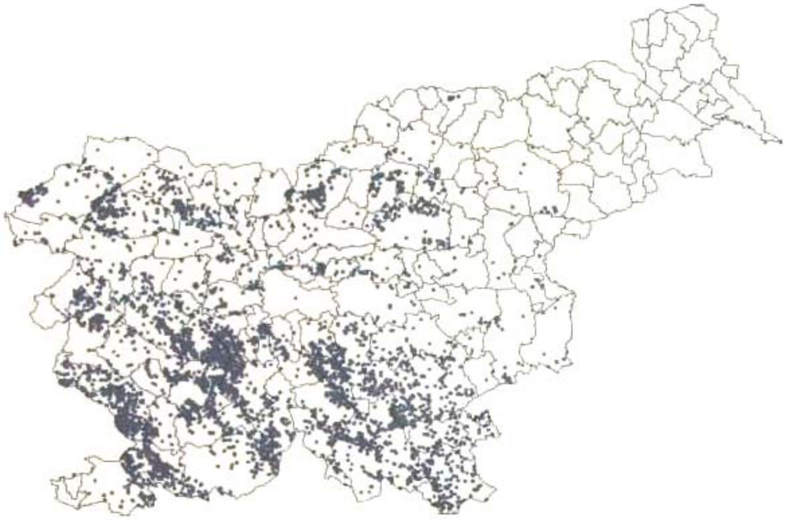


Figure 3: Contaminated and damaged caves according to the register of caves

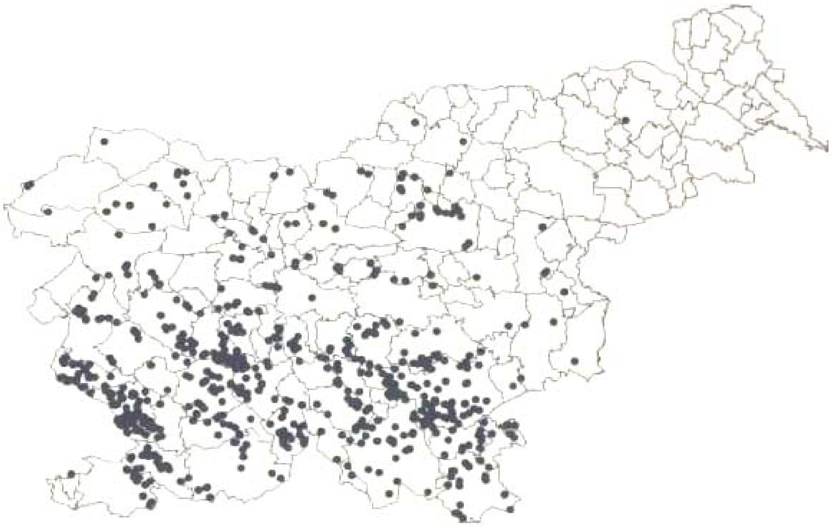


Figure 4: Caves contaminated with organic waste

Figure 5: Caves recorded as active waste disposal sites, caves filled with waste, and caves that have been cleared

Figure 6: Destroyed or mechanically damaged caves

Table 1: Types of waste that were or still are being dumped in karstic caves

Total contaminated or damaged caves	694
No data on type of waste	109
Cave is active waste disposal site	58
Cave filled with waste	57
Cave is destroyed (it no longer exists)	15
Cave is damaged	12
Cave is cleared up	2
Mixed, mostly municipal waste	333
Carrion	85
Animal bones	31
Human bones	48 (71)
Faeces	6
Waste of vegetable origin	25
Building materials	15

The types of waste are known, but the quantity of the dumped waste is unknown since no records on the duration of the dumping exist.

Concern for the clear-up of the contaminated caves is negligible and the state is not investing sufficient funds to eliminate the consequences of contamination where this is still possible. In some cases local communities have been doing this but in the majority of cases the situation remains unchanged although the National Environmental Action Programme states that the priority programmes include the clear-up of obsolete landfills as well as the restoration of destroyed or damaged natural resources and areas.

3. KEEPING RECORDS OF INDUSTRIAL WASTE LANDFILLS

Between 1998 and 2000, the regulator, i.e. the Ministry of the Environment and Spatial Planning, drew up the records of industrial waste landfills. It covered 27 locations of major industrial waste landfills, which are mainly located in the closest vicinity of industrial plants from which the waste originates. It has been established that 13 industrial waste landfills exist in these locations, which means that a landfill with one type of waste may be located in several places in the closest vicinity of industrial plants. One sector of industry thus used and still uses several locations for dumping the waste, and these locations are marked as one landfill if they only contain waste from one sector of industry. In drawing up the records, the following data has been taken into account: general data on the source of waste and the manager of the site, description of the site, waste management data, data on natural features of the location, data on the implemented technical measures. On the basis of the data, conclusions were drawn up containing priority assessments of the required clear-ups and an assessment of what legislative adjustments are needed with respect to the year the dumping was stopped.

According to Slovenian legislation (Waste Disposal Rules, *Official Gazette RS*, no. 5/2000) waste must be classified by properties, i.e. into dangerous industrial waste or not dangerous or inert industrial waste.

Table 2: The list of recorded industrial waste landfills on 27 locations.

No.	Waste generator	Landfill designation
1	Šoštanj coal-fired power station – old	landfill of fly ash, slag and products of additive desulphurisation of flue gases
2	Šoštanj coal-fired power station – new	landfill of products of desulphurisation of flue gases
3	Trbovlje coal-fired power station	landfill of fly ash and slag
4	Zagorje Mine – undergoing closure	filling up the depression along the Hotedrščica stream
5	SŽ Acroni d.o.o. –Javornik	Javornik tailings disposal site
6	SŽ Acroni d.o.o. – Bela	Bela tailings disposal site
7	Slovenian ironworks – Metal Ravne	Ravne tailings disposal site
8	Slovenian ironworks – Jeklo Štore	Rehabilitation of Vrhe nad Štorami gravel pit
9	TDR – Metalurgija d.d.	Industrial waste landfill
10	Mežica MPI d.o.o. mine	Metallurgic slag and crushed artificial substance
11	Talum d.d. Kidričevo – active	fly ash landfill
12	Talum d.d. Kidričevo – not active	red silt landfill
13	IMP Livar d.d.	Suhi Most Polževo waste disposal site
14	ETA d.d. Cerkno	industrial waste landfill in Novaki
15	Snaga d.o.o. public company	Metava landfill of special waste
16	Salonit Anhovo gradbeni materiali d.d.	Landfill of waste asbestos and cement material
17	LKI Lesonit d.d.	wood waste landfill
18	IGM Sava d.o.o.	Stari Grad gravel pit
19	Paloma d.o.o.	industrial waste landfill
20	Industrija Usnaj Vrhnika d.d.	waste disposal site of Šmartno Rakovnik tannery
21	Sugar factory – green waste	waste disposal site – composting of green waste
22	Sugar factory – solid waste	soil and stone landfill
23	Petrol d.d. Ljubljana	tar landfill
24	TKI Hrastnik d.d.	industrial waste landfill of the Unično waste disposal site
25	TOK in bankruptcy	waste disposal site of the organic acids factory
26	Celje zinc plant – Bukovžlak	Bukovžlak gypsum landfill
27	Celje zinc plant – Žepina	solid waste landfill with soil barrier in Žepina

The table shows the types of waste, which were or still are being dumped on industrial waste landfills, as well as the fact that certain locations are in the closest vicinity of the same industrial complexes.

Analysis of the data collected demonstrates the following conclusions:

- in 1998, 1,406,000 tons of industrial waste was dumped in the landfills indicated;
- the majority of waste is generated by the energy sector, i.e. 80 per cent (the Šoštanj coal-fired power station and the Trbovlje coal-fired power station);
- by 2005 the expected quantity of waste generated by industry will increase by 20 per cent, i.e. to some 1,650,000 tons, mainly in coal-fired power stations;
- the iron industry, non-ferrous metal industry and metal processing industry will see a decrease in the quantity of waste;
- the surface of all locations of the recorded industrial waste landfills amounts to 245 hectares with some 35 million of waste dumped so far;
- in the majority of cases, the terrain of the sites was not protected, which means that waste was dumped directly on the ground surface;
- the recorded landfills have the capacity for another 15 million tons of waste;
- clear-ups of landfills at risk (due to terrain configuration, geological composition of the soil, climate conditions or vicinity of urban settlements, etc) need to be started.

Table 3: The expected closure of industry-generated waste landfills by the end of 2002

Serial no.	No.	LANDFILL HOLDER	Annual amount of waste envisaged for dumping in tons or m^3	Year of closure	Legal status
1	10	Mežica MPI mine	4,275 m^3	1999	Illegal
2	11	TALUM d.d. KIDRIČEVO – active	1,000 t	2000	Illegal
3	4	Zagorje mine – being closed	30,000 m^3	~2001	Legal

Table 4: The expected closure of industry-generated waste landfills by 2003

Serial no.	No.	LANDFILL HOLDER	Annual amount of waste envisaged for dumping in tons or m^3	Year of closure	Legal status
1	16	SALONIT Anhovo	1,000 t	2003	legal
2	24	TKI Hrastnik	3,500 t	~2002	legal
3	19	PALOMA	10,800 m^3	~2002	illegal

Table 5: Industry-generated waste landfills that will operate until 2004, or that will have to be equipped with a system for collection and treatment of leachate

Serial no.	No.	LANDFILL HOLDER	Annual amount of waste envisaged for dumping in tons or m^3	Year of closure	Legal status
1	3	TE Trbovlje	250,000 t	~2004	legal
2	8	SŽ Jeklo Štore	18,638 m^3	2004	illegal

Table 6: Industry-generated waste landfills that will have to be equipped and aligned with the Waste Management Rules by 2008, and which are expected to operate until 2015 or longer

Serial no.	No.	LANDFILL HOLDER	Annual amount of waste envisaged for dumping in tons or m^3	Year of closure	Legal status
1	1	TE Šoštanj – old	896,400 t	~2020	illegal
2	2	TE Šoštanj – new	896,400 t	>2020	legal
3	5	SŽ Acroni Javornik	8,712 m^3	2010	legal
4	7	SŽ Matal Ravne	20,330 m^3	2010	illegal
5	14	ETA Cerkno	5,475 m^3	2019	legal
6	15	JP Snaga	550 m^3	2030	legal
7	16	LKI Lesonit	2,300 m^3	2020	illegal
8	9	TDR Metalurgija	15,040 m^3	~2015	illegal
9	20	IUV Vrhnika, PE Šmartno	1,200 t	~2010	illegal

Table 7: Industry-generated waste landfills whose final capacities are not known and that therefore have an undefined life span.

Serial no.	No.	LANDFILL HOLDER	Annual amount of waste envisaged for dumping in tons or m^3	Year of closure	Legal status
1	13	IMP Livar	7,100 t	Non-defined	illegal
2	18	IGM SAVA – VIDEM KRŠKO	47,661 m^3	Non-defined	legal
3	21	TSO Ormož, green waste	23,000 t	Non-defined	legal
4	22	TSO Ormož, solid waste	7,600 t	Non-defined	illegal

Table 8: Industry-generated waste landfills that have already been closed but require monitoring.

Serial no.	No.	LANDFILL HOLDER	Annual amount of waste envisaged for dumping in tons or m^3	Year of closure	Legal status
1	6	SŽ Acroni Jecenice, Bela Repeated dumping expected	No data	1998	legal
2	12	Talum d.d. Kidričevo, inactive landfill of red silt		1991	illegal
3	23	Petrol d.d. Ljubljana – tar landfill		1982	legal
4	25	Organic acids factory		1991	illegal

Conclusions of records on industry-generated waste landfills:

- industry-generated waste landfills records have shown the issues that have not yet been addressed, and problems that the industry will have to resolve with the help of the state;
- the records have shown the amounts and types of industry-generated waste, as well as the capacities of landfills that could be used in the future;
- the records have shown the issues that will have to be resolved (leachate, protection of soil, etc.) in order to protect the environment in which landfills are located;
- legislation aligned with EU law must provide a different method of waste disposal, which will increase costs;
- landfills in the process of closure must be dealt with as old burdens, which will have to be regulated so that they will not pose a risk to the environment, and their situation adjusted to new regulations.

4. CONCLUSIONS

Environmental policy documents and legislation aligned with EU guidelines and directives have been focused on the resolution of current problems as well as old burdens. They include the clear-up of karstic caves where waste has been dumped, and the clear-up of the industry-generated waste landfills. So far the regulator has only been addressing these issues on a declarative level while the application is very rare or practically non-existent. With Slovenia's accession to the EU, these issues will soon have to be addressed differently, given the commitments and promises signed in the pre-accession statement, as well as the damage sustained by the environment.

5. REFERENCES

1. Encyclopaedia of Slovenia, Volume 5, Založba Mladinska Knjiga, Ljubljana 1991

2. Register of Caves in Slovenia

3. National Environmental Action Programme, the Ministry of the Environment and Spatial Planning, the Administration of the RS for the Protection of Nature, Ljubljana, December 1998

4. Final Report on the Inventorying of Landfills in the Republic of Slovenia, 1999, the Ministry of the Environment and Spatial Planning; http//www.gov.si/uvn/slo/datoteke/okolje/odlagalisca

5. Waste Disposal Rules*, Official Gazette RS*, no. 5/2000

SPAIN

The information in this tour de table is current as of January 2002.

NATIONAL FRAMEWORK TO MANAGE CONTAMINATED SOILS IN SPAIN

LEY 10/1998, De Residuos (Waste Act)

Boe 22 - April 1998

Title V: Polluted Soils
    Art.27. Contaminated soils declaration
        Art. 28. Mending of environmental hazards due to soil pollution.

Functions of the Administrations

- Ministry of Environment:

  -Legislation
  -Coordination of Regional Governments

- Regional Governments (17)

  -Executive Activities:

    Investigation
    Inventory
    Register
    Priorisation of Sites
    Projections
    Remediation

- Municipalities

  -only urban wastes landfields

Waste Act

Art. 27. Contaminated Soil Declaration.

- Regional Governments are responsible for the elaboration of an inventory of those soils/sites with high risk of threat for human health and environment.
- Criteria and standard to declare a soil as contaminated are setting up by the Central Government, based in reuse of soils.
- The declaration of one area as a contaminated soil will force to carry out the necessary actions to its cleaning and recovery, previous request of the Regional Authorities.
- The owner of the pollutant activity has always the liability to clean up the soils.
- When the site is public property its remediation is financed with public funds.
- National Plan for Remediation of Contaminated Soils (1995-2005)
- National Government is responsible for the elaboration of a list with all those economical/ industrial activities which potentially can produce soil pollution.
- The declaration of one area as a contaminated land would be included as a marginal note in the Property Register.

Potentially Pollutant Activities

- Compulsory Declaration by the owner
- Included in the property register
- Situation report every year
- Ministry is making a decree
  - -list of “a Priori” Pollutant activities
  - -hazardous substances landfields
  - -low pollutants activities are excluded

Criteria and Standard to Declare a Soil as Contaminated

- Three classes of soils
  - -not contaminated
  - -contaminated
  - -potentially contaminated
- Due to concentration of some substances and heavy metals
- Risk
- Soil reuse after cleaning up

Table 1: Guideline Levels

Substance	CASRN	Industrial use	Residential Use	Without Restrictions on use		
				Soil Organism	**Organismos acuáticos**	**Vertebrados terrestres**
			(mg/Kg soiil)			
1,1-Dicloroetileno	75-34-3	100***	70**	0,01(*)	0,034	
1,1,2,2-Tetracloroetileno	79-34-5	3**	0,3**	0,014	0,01(*)	
1,1,2-Tricloroetano	79-00-5	10**	1**	0.11	0.37	
1,2-Dicloroetano	107-06-2	5**	0,5**	0,35	0,05	0,44
1,2-Diclorobenceno	95-50-1	100***	70***	0.021	0.1	3.3
1,2-Dicloropropano	78-87-5	4	0,5**	4,24	0,06	1.5
1,3-Dicloropropeno	42-75-6	7**	0,7**		0,01(*)	0.11
2-Clorofenol	95-57-8	100***	10**	0,01(*)	0,01(*)	
2,4,5-Triclorofenol	95-95-4	100***	100***	0,02	0,05	0.5
2,4,6-Triclorofenol	88-06-2	90**	9**	0.15	0,01(*)	0.2
2,4-Diclorofenol	120-83-2	10**	1**	1.5	0,06	0.40
1,2,4-Triclorobenceno	120-82-1	90**	9**	0.05	0.12	14.7
1,4-Diclorobenceno	106-46-7	40**	4**	0.096	0.10	0.35
1,4-dioxano	123-91-1			29	0.27	
Acenafteno	83-32-9	100***	60**	0,05	0,01(*)	
Acetona	67-64-1	100***	10**		0,01(*)!	#¡16.60
Aldrin	309-00-2	1**	0,1**	0,01(*)	0,05	0.09
Antraceno	120-12-7	100***	100***		1,4	100***
Benceno	71-43-2	10**	1**	0.1	0.17	2.54
Benzo(a) antraceno	56-55-3	20**	2**	3.8	0.23	
Benzo(a)pireno	50-32-8	2**	0,2**	0.15	15	22
clordano	57-74-9	1**	0,1**	0.024	0.01(*)	0.4
Clorobenceno	108-90-7	35	10**	1	0.1	
Cloroformo	67-66-3	25	5**		0,08	
Dieldrin	60-57-1	1**	0,1**	0.13	0.15	0.01(*)
Endrin	72-20-8	1**	0,1**	0.01(*)	0.01(*)	0.01(*)
Etilbenceno	100-41-4	100***	20**		0,01(*)	2.7
Fenol	108-95-2	100***	100***	0.05	0.01(*)	1.65

Table 2: Guideline Levels of Soil Use

EXPOSURE CENARIOS	Residential	Industrial	Without Restrictions
Soil vapours inhalation	●	●	●
Soil Particles inhalation	●		●
Accidental ingestion of polluted soil	●	●	●
Ingestion of contaminated food	●		
Skin contact with polluted soil	●		●

National Plan for Remediation for Polluted Soils

1. 1995-2005
2. ministry of environment 50%
3. regional governments 50%
4. R.G. lead the activities
5. Public Property sites
6. Inventory 2 steps: 4.900 sites

Waste Act

Art. 28. Mending of environmental hazards due to soil pollution

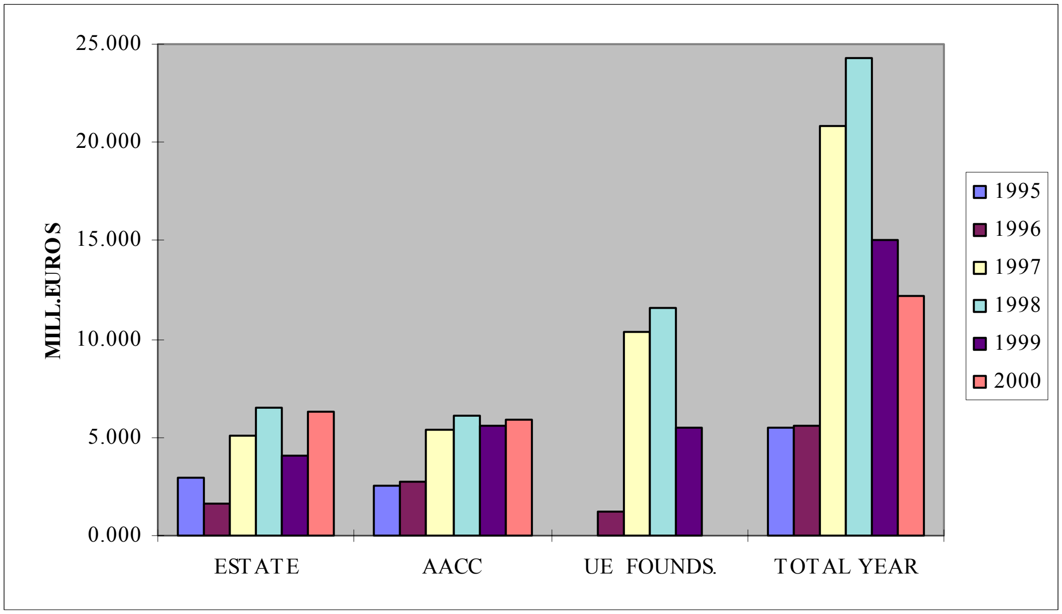
Cleaning and recovery could be carried out through voluntary agreements between the pollution responsible or through collaboration agreements with the competent authority.

Remediation of Polluted Soils

- Polluter pays
- Subsidies to prevention
    -NPHW
    -Minimization
    -End of line treatment of hazardous wastes
    -Clean up technologies
- Ministry of environment + regional governments can loan to private for remediation
- Agreements mimam-regional governments
- Return normally with profit in 10-15 years:
    -In cash
    -In lands
    -Housing

Table 3: Total from 1995-2000

YEAR	ESTATE	AACC	UE FOUNDS.	TOTAL YEAR
1995	2,909	2,548		5,457
1996	1,593	2,753	1,202	5,547
1997	5,103	5,415	10,361	20,879
1998	6,497	6,136	11,636	24,275
1999	4,021	5,547	5,505	15,073
2000	6,269	5,920		12,189
TOTAL	26,392	28,319	28,704	
TOTAL PLAN				83,420


25.000
20.000
15.000
10.000
5.000
0.000
MILL.EUROS
ESTATE
AACC
UE FOUNDS.
TOTAL YEAR
1995
1996
1997
1998
1999
2000

SWITZERLAND

1. SUSTAINABLE REMEDIATION OF CONTAMINATED SITES

A. Situation of Contaminated Land in Switzerland

In Switzerland there are some 40,000 to 50,000 polluted sites to register (landfills, industrial and commercial sites as well as accident sites) of which some 3000 are considered to be in need of remediation and thus classified as contaminated sites. Although Switzerland had no significant mining industry, hardly any heavy industries, no war-related contamination and a long tradition of incinerating urban waste, the contaminated land management has a high priority due to the coincidence of a big number of contaminated sites in the immediate neighbourhood of highly vulnerable groundwater and a high population density in the Swiss central plateau. The main natural resource affected is groundwater and therefore often the public supply of drinking water.

B. Swiss Contaminated Land Legislation and Politics

The urgently necessary legal security for the uniform management of contaminated sites throughout the whole of Switzerland has been stipulated in 1995 by the amendment to the Law relating to the Protection of the Environment (1983) and later in 1998 the Contaminated Site Ordinance (CSO). The goal of these regulations is to clean up the ”sins of yesterday” within the next 20 to 30 years in order to hand over as little environmental encumbrance as possible to future generations. The bill for these remediations amounts to over 3 billion €. With the Ordinance relating to the tax for the remediation of contaminated sites (OTRC) the government is able to support the remediation of orphan sites as well as urban landfills with 20 million € per year.

The goal of remediation is to stop emissions from a contaminated site to such an extent that over the long-term no need for remediation exists; one has to achieve a long-term, sustainable elimination of the danger. It is unacceptable that a site must be subjected to intensive monitoring or cost-intensive treatment of waste water or air over many generations. But that doesn’t mean that every remediation requires removal of the pollutants from the site.

The Contaminated Site Ordinance accepts, that the objectives of remediation shall either be achieved by:

- the elimination of environmentally hazardous substances (decontamination); or by
- preventing and monitoring the diffusion of environmentally hazardous substances in the long term (containment); or
- with respect to hazard for the soil fertility, the restriction of the use of that soil.

C. Decontamination Versus Containment

At first glance, containment seems to be cheaper than decontamination in any case. But, in establishing containment measures, protection of the environment is only guaranteed as long as the sealing-, drainage- and treatment-systems are in function. Attention must therefore be paid also to the cost of the long-term maintenance, monitoring and repair or even restoration of the whole system. For that reason the CSO requires for containment measures the securing of these overall necessary financial means and - based on the principle of sustainability - that the site could be left to its own devices without any further need for treatment after a period of no more than one to two generations. Containment is therefore only accepted by the Swiss legislation, where the pollutants are easily degradable or long-term-adsorbed, as it may be the case e.g. in domestic waste landfills or at sites contaminated by mineral oils.

The natural degradation of persistent organic pollutants as well as the legally acceptable washing out of hazardous heavy metals in landfills or industrial sites may require up to several hundred years.

Contaminated sites containing a high proportion of such substances are therefore named as "Persistent Pollutants Sites" or PEPSI's. Containment systems for PEPSI's would need to be monitored and maintained for many hundred years. Such sites have to be remediated by decontamination mesures.

The following table summarises the advantages and disadvantages of containment and decontamination:

containment of PEPSI's	**decontamination of PEPSI's**
environmental risks persist over a long time span	environmental risk removed
low initial investment costs for construction of sealing-, treatment- and monitoring systems	high initial investment costs for excavation, waste treatment, re-depostion, recultivation
long-term costs for water and air treatment, maintenance and replacement of the systems, risk for unexpected break-downs of the systems, monitoring	no follow-up costs
use-restrictions over long periods	immediate re-use of the property possible
polluter-pays-principle not ascertained	polluter-pays-principle directly applicable
financial risk has to be carried by the public	financial risk has to be carried by polluters (eventually banks)
not sustainable	sustainable

The Swiss contaminated sites policy therefore postulates a differentiated clean-up strategy:

- if the hazardous substances that cause the need for remediation will be degraded within the fixed time for clean-up **monitoring of the contaminated site** (so-called "monitored natural attenuation") is accepted;
- if the hazardous substances that cause the need for remediation will be degraded within 1-2 generations **containment measures** are accepted**;**
- if the hazardous substances that cause the need for remediation are persistant and will not be degraded within 1-2 generations **decontamination of the site** is mandatory.

2. INTRODUCTION

Since July 1997, the Law on the Protection of the Environment has contained regulations on the remediation of polluted sites. The Contaminated Sites Ordinance, in force since October 1998, stipulates how this part of the law is to be implemented. These provisions specify the principles of what measures must be taken at polluted sites, when they must be taken, who has to take them and who has to pay for them.

3. WHO TAKES THE MEASURES?

The person who must carry out measures (investigations, monitoring, remediation) at polluted sites is not always the same as the person who must bear the costs of those measures. Therefore, in dealing with polluted sites, a distinction has to be made between the obligation to take measures, and the obligation to bear the costs.

The Contaminated Sites Ordinance states that, in principle, measures are to be carried out by the holder of the site. The term "holder" is not clearly defined from the legal point of view. However, here the holder may be for instance the tenant, the leaseholder or another person, who has a close link to the site. This imprecise term has the advantage that there is always a holder, whom the authorities may oblige to implement the measures.

As is the case for all principles, there are certain exceptions to the principle that the holder of the site has to take the measures. The authorities may also oblige third parties (not holders) to carry out preliminary investigations, monitoring or detailed investigations, if there is reason to assume that the pollution of the site was caused by their behaviour. However, for working out the remediation project and carrying out the remediation measures, the authorities may only oblige third parties to take measures if it is certain that the pollution was caused by their behaviour.

Before obliging a third party to carry out measures, the authorities have to obtain the approval of the holder. Usually, this will not represent any problem, because the holder will not have to finance the measures himself/herself in advance.

4. WHO BEARS THE COSTS?

After it has become clear who must take the measures, the next question is who must bear the costs of the measures. The polluter pays principle is established here, which means that the person who has caused a measure to have to be taken must bear the costs.

The central question here is who is considered to be a polluter. Here it will be distinguished between two types of responsible persons: persons responsible by their behaviour, and persons responsible by virtue of their position.

A person who is responsible by behaviour is anyone who caused pollution through his/her own behaviour or the behaviour of a third party, which took place under his/her responsibility.

A person who is responsible by position is anyone who has legal or actual power over the matter that causes the illegal situation. In the area of polluted sites, this is the holder of the site (owner, leaseholder, tenant, etc.).

According to the Law on the Protection of the Environment, if several responsible parties are involved, they have to bear the costs according to their respective shares in the responsibility. Persons responsible by behaviour are primarily responsible, and those responsible by virtue of their position are only considered as secondarily responsible. There is no joint and common shared responsibility among different responsible persons. Therefore, if a responsible person no longer exists, the others do not have to bear additional costs.

Following on from the polluter pays principle and from the fact that different responsible persons are not jointly and commonly liable, in cases in which a person responsible by behaviour is no longer available or able to pay, the resultant costs are transferred to the communities responsible for execution. In such cases, the cantons will normally have to bear the costs.

The Law on the Protection of the Environment, also expressly states that the holder of the site is completely freed from having to bear costs as the person responsible by position, if he/she had no knowledge of the pollution, and gained no advantage form the pollution or from the remediation.
It is furthermore established that the authorities have to decide on the distribution of costs, if those responsible for carrying out remediation measures require this, or if the authorities perform the remediation themselves.

5. THE FEDERAL GOVERNMENT’S FUNDING SOLUTION

In Article 32e of the Law on the Protection of the Environment, the legislator gave the Federal Council the competence to levy a tax on the deposit of waste, and to use the proceeds to pay the cantons part of the remediation costs. The Federal Council made use of this competence by means of the Ordinance concerning the Tax for the Remediation of Contaminated Sites. Since 1 January 2001, a tax has been levied on the deposit of wastes. From the year 2002, using the proceeds from this tax, financial contributions will be made to the cantons for the remediation of landfill sites for municipal waste and other contaminated sites. However, the cantons will only receive federal contributions if the costs actually accrue to them, for instance in the case of landfill sites for municipal waste, for which they have an individual responsibility (they are regarded as responsible), and for sites where there are costs for the canton because the responsible person can no longer be prosecuted. The level of the federal contributions amounts to 40 percent of the remediation costs.

6. CONCLUSIONS

As regards the implementation of measures, Switzerland has chosen a system which guarantees that the measures are taken as quickly as possible. A holder of the polluted site always exists, and the authorities may oblige him/her to carry out the measures. However, if appropriate, the authorities may also oblige third parties, provided that this will ensure that the measures are carried out.

TURKEY

The information in this tour de table is current as of January 2002.

1. LEGAL AND ADMINISTRATIVE ISSUES

There is a growing recognition of soil and groundwater pollution problems in Turkey since the enforcement of the regulations of the *Control of Solid Wastes (C of SW)* in March 1991 and *the Control of Hazardous Wastes (C of HW)* in August 1995. The main purpose of these regulations is to provide a legal framework for the management of municipal solid wastes and hazardous wastes throughout the nation. They basically regulate the collection, transportation, and disposal of wastes that can be harmful to human health and the environment and provide technical and administrative standards for construction and operation of disposal sites and related legal and punitive responsibilities.

C of SW and *C of HW* regulations have been recently subjected to some modifications in 1998 and 1999, respectively. However, these changes are mostly related to some management and technical aspects of waste collection, reuse, and disposal activities and have no implications related to contaminated sites. There are a couple of new legislative proposals, which will most likely have same impact on contaminated sites. The first of these proposals is about *local governments and municipalities,* and the second one is about preparation of a regional "*Environmental Emergency Response Plans*." With the first legislative proposal, local governments and municipalities will have explicit authority and responsibility for planning, building and operating the new solid waste disposal sites and rehabilitating the old ones. Considering that a large number of contaminated sites are in fact the old waste dumpsites, it is expected that the new legislative proposal will have a positive impact on rehabilitation of contaminated dumpsites. This new proposal also provides new financial tools for generating funds to fulfill the assumed responsibilities. The second proposal will make the industrial facilities responsible for preparing their own emergency response plans and get these plans approved by the local authorities. Thus, this new legislative proposal will provide a framework for systematic approach for identification, registration and rehabilitation of contaminated sites on regional basis. Another recent development has been related to a proposal for amending the Environmental Law. This amendment proposes specific articles related to issues of soil contamination and clean up of contaminated land.

2. REGISTRATION OF CONTAMINATED SITES

Existing regulations do not explicitly define the concept of contaminated sites. For example, the *Control of Hazardous Wastes* defines what a hazardous waste is and provides lists categorizing hazardous wastes based on their sources, chemical compositions and accepted disposal techniques. Thus, any site contaminated with or subjected to any of these categorized hazardous wastes can implicitly be defined as a contaminated site. However, difficulties arise from the lack of information for most of chemicals in these lists regarding specific maximum concentration levels (MCLs) or remedial action levels.

Currently, identification of any contaminated site is not based on a certain systematic approach. These sites are mostly identified after some potential environmental problems become obvious and public as a result of the efforts of local authorities or concerned citizens. However, some current policy developments by the Ministry of Environment can make the identification of contaminated sites somewhat more systematic. In this new policy development, the waste management commission, an administrative body proposed by the *Control of Hazardous Wastes* regulation, initiates preparation of industrial waste inventory on a regional basis. Waste inventory is planned to be achieved by requiring all the industry to fill out *annual waste declaration forms* revealing the type, amount, composition and the current disposal practice of their wastes. This way, it is expected that waste generation activities and pollution potentials of industries can be monitored; regionally effective waste reutilization and recycling programs can be implemented; and finally regional needs for the type and capacity of waste disposal facilities can be identified. In response to such efforts, an integrated waste management facility, including a landfill and incineration unit for disposal of industrial wastes, is becoming operational at full scale in heavily industrialized Marmara region.

Another policy development related to identification of contaminated sites is the work progressing towards the preparation of a “Soil Pollution Control” regulation. It is expected that this regulation will clarify the existing confusion over the remedial action and cleanup levels and set a guideline for the selection of appropriate cleanup technologies for various different types of contaminated soil sites.

3. REMEDIAL METHODS IN USE

Currently, there are no reliable and comprehensive case study based statistics or data on remedial methods and technologies used for cleanup of soil and groundwater in Turkey. Regulatory aspects of acceptable remedial methods and technologies are provided by the Control of Hazardous Wastes regulation, which specifies acceptable remedial and/or disposal methods for a given type of contaminant group. In the Control of Hazardous Wastes regulation, acceptable methods for a large number of contaminant group is given as physical, chemical and biological treatment without stating the specific name of the method. However, it clearly states that use of remedial technologies is a must for wastes containing a large group of contaminants. Currently, there is no official knowledge regarding the widespread past use of particular technologies for soil and groundwater cleanup in Turkey. However, it is known that land farming and at few chemical spill site pump-and-treat type technologies are being used for waste treatment and groundwater cleanup. Most probably these sites will set precedence, in terms of both cost and performance, for cleanup in other similar sites.

4. RESEARCH AND DEVELOPMENT ACTIVITIES

There is a pressing need for research and development of soil and groundwater cleanup technologies in Turkey. Some research is being conducted by private sector to develop equipment for field applications of air sparging and soil vapor extraction systems at gas stations.

5. CONCLUSIONS

There is a growing recognition of soil and groundwater degradation problems in Turkey. Because the enforcement of hazardous waste regulations is relatively new, some difficulties in the identification of soil and groundwater contamination sites remain unresolved. Recent regulatory efforts are helpful for identification of these sites contaminated as a result of past activities. In the near future a considerable increase in the number of registered contaminated sites is expected.

Turkey presently relies heavily on surface water resources to satisfy water supply demands mainly because of relative abundance of surface waters resources. Groundwater constitutes a relatively small component of total available resources (17 percent) but it represents a significant portion (27 percent) of total water withdrawal. However, due to growing water demand parallel to rapid population and industrial growth, an increasing demand for food production, urban expansion and accelerated degradation of surface water quality, protection of clean groundwater resources as well as remediation of contaminated soil and groundwater sites are becoming environmental issues of high priority. The sustainable development of groundwater resources requires proper waste treatment for communities and industrial plants. Groundwater is the major source of drinking water supply and as such needs to be fully protected and allocated only for high quality uses. Although legislation on groundwater exists, their protection appears to be neglected at least in certain areas. With the spread of irrigation practices, the pollution threat to groundwater is also increasing. To date, unsatisfactory efforts have been made to protect groundwater from the increasing variety of potential pollution sources, such as agricultural chemicals, septic tanks, and waste dumps. The control of soil and groundwater contamination is essential to Turkey’s on-going reliance on groundwater resources for potable water.

The management of municipal and hazardous wastes in Turkey is inadequate to ensure proper handling and treatment. Industrial waste, particularly hazardous waste, has grown proportionately with industrial production. Treatment facilities are minimal and their disposal is usually haphazard. They pose serious dangers for soil and groundwater and in some cases for public health. The legal gap has to a certain extent been filled with the regulation of the Control of Hazardous Wastes. Minimization of the generation and availability of facilities for proper storage and disposal of hazardous wastes has been embodied in this Turkish regulation. The policies are being strengthened by the application of such mechanisms of industrial waste management as the full implementation of environmental impact assessment for new proposals, the requirement that waste management programs be prepared and implemented by existing industries, and the encouragement of waste reuse.

UNITED KINGDOM

The information in this tour de table is current as of January 2002.

This is an update to the Tour de Table papers presented at the Vienna Meeting (February 1998), the Angers Meeting (May 1999) and Wiesbaden meeting (June 2000) of the Pilot Study.

1. LEGAL AND ADMINISTRATIVE ISSUES

Background to UK policy on land affected by contamination and the role of the “contaminated land provisions” of Part IIA of the Environmental Protection Act 1990 (“the 1990 Act”) have been described in the previous Tour de Table papers. On 1 April 2000, the 1990 Act came into force in England. The Secretary of State for the Environment, Transport, and the Regions also made the Contaminated Land (England) Regulations 2000 under provisions of specific parts of the 1990 Act. Detailed information on the implementation of the 1990 Act in England can be found in Department of Environment, Transport, and the Regions (DETR) Circular 02/2000 [1]. The Circular aims to:

- Promulgate guidance to regulatory authorities on how specific parts of the 1990 Act should be interpreted and the scope of any assessment that they must make. The guidance covers the definition and identification of contaminated land, the remediation of contaminated land, and the apportionment of liability and issues of cost recovery. It is an essential part of the new regime.
- Set out the way in which the new regime is expected to work, by providing a summary of Government policy in this field, a description of the new regime, and a guide to the Regulations.

The responsibility for implementing the 1990 Act in Scotland and Wales rests with the Scottish Executive and the National Assembly for Wales, respectively. In Scotland, this Act was implemented in July 2000, whilst in Wales, it was implemented more recently.

After implementation of Part IIA in April 2000, Local Authorities were required to prepare and publish a written strategy for inspecting their areas as a means of identifying contaminated land. The Environment Agency has supported this task by providing relevant information that it holds already. To date, 85% of the Local Authorities in England are reported to be either consulting formally on their inspection strategy or have published it. It is expected that most of the remaining draft strategies will be published by the end of September 2001.

After an inspection strategy has been published, the Local Authority is required to inspect its area from time to time, in line with its written strategy in order to identify any land that meets the statutory definition of contaminated land. The Environment Agency is currently aware of 19 contaminated land determinations in England of which 4 are special sites (i.e. sites where it is likely that the Agency will be the regulator). In addition, the Agency is currently involved in inspecting a further 19 potential special sites.

2. TECHNOLOGY DEVELOPMENT PROGRAMMES

Technology development programmes that support the development of innovative methods for dealing with land remediation are summarised below in table 1.

3. REMEDIAL METHODS IN USE

At the last Pilot Study meeting in Wiesbaden, Germany, it was reported that the Environment Agency had commissioned a survey of remedial techniques that had been used in England and Wales for remediation during the period January 1996 to December 1999. This survey has now been published [3].

Table 1: Technology development initiatives for land remediation in the UK

Programme	Objective	Progress	Contact details
CLAIRE (Contaminated Land: Applications in Real Environments) 1998 to present	To establish a network of test sites within the UK to research and demonstrate cost-effective techniques for the investigation and remediation of land affected by contamination.	1. Identified 45 potential sites; 2. 25 project applications received in which 11 have been ratified; 3. Demonstration projects include: • Soil washing • Slurry bioreactors to treat coal tar and PAH contaminated soils.	www.claire.co.uk
exSite 1998 to present			
Bioremediation LINK Programme (Jointly sponsored by the Dept. of Trade and Industry, BBSRC, EPSRC and the Environment Agency) Programme announced 1April 2001	To support the development of technologies that will provide UK industry with the multidisciplinary capability necessary to exploit biotechnology in remediating contaminated land and water. Focus areas include: • Natural attenuation in groundwater and soil; • Engineering *in situ* bioremediation; • Process scale-up to field conditions; • Bioremediation within a risk management framework; • Monitoring methods for understanding *in situ* bioremediation;	Call for the first round of proposal outlines now closed.	Dr Howard Simons, LGC Link Secretariat, hs2@lgc.co.uk
Faraday Centre for Remediation of the Polluted Environment (A consortium consisting of 7 UK universities, 4 technology transfer organisations, and the Environment Agency).	To support research in developing new technologies to remediate land contamination and to disseminate widely the information generated through practical training and networks. Priority areas have been identified that include: • Natural & enhanced attenuation of subsurface pollutants; • Biological site characterisation tools; • Application of permeable reactive barriers in the UK; • Process flowsheet optimisation for soil and water remediation.		

4. RESEARCH AND DEVELOPMENT ACTIVITIES

Table 2 lists a number of completed, on-going, and proposed R&D projects related to the remediation of land affected by contamination funded by the environmental agencies and the research councils.

Table 2: UK R&D Projects on remediation of land affected by contamination (not intended to be inclusive)

PROJECT	STATUS
RESEARCH COUNCILS (BBSRC – Biotechnology and Biological Sciences Research Council; EPSRC – Engineering and Physical Sciences Research Centre; NERC – Natural Environment Research Council)	
Bioremediation: a study of stakeholders attitudes	BBSRC Dr Kate Millar, University of Nottingham
Dual anaerobic system for bioremediation of metal/organic wastes	BBSRC Professor Macaskie, University of Birmingham
Bioremediation and microbial population dynamics	BBSRC Dr Head, University of Newcastle
Cyanide biodegradation: a model for the development of molecular probes for optimisation of bioremediation	BBSRC Professor Knowles, University of Oxford
Phytoremediation: an integrated biological approach to decontamination of polluted soils	BBSRC Professor Thompson, Centre of Ecology and Hydrology (CEH)
An integrated, multifunctional system for bioremediation of waters containing xenobiotics and toxic metals	BBSRC Professor Livingston, Imperial College of Science, Technology, and Medicine
Processes controlling the natural attenuation of fuel hydrocarbons and MTBE in chalk	EPSRC Professor David Lerner, University of Sheffield
Non-invasive characterisation of NAPL-contaminated land by spectral induced polarisation (SIP) tomography	EPSRC / NERC Dr Ogilvy, British Geological Survey
New sensor system for monitoring solvent migration from contaminated sites	EPSRC/NERC Professor Williams, University of Central London
Studies into metal speciation and bioavailability to assist risk assessment and remediation of brownfield sites in urban areas	EPSRC/NERC Professor Thornton, Imperial College of Science, Technology, and Medicine
In situ sensing of the effect of remediation on available metal fluxes in contaminated land	EPSRC/NERC Professor Davison, University of Lancaster
Bacterial biosensors to screen in situ bioavailability, toxicity, and biodegradation potential of xenobiotic pollutants in soil	NERC Professor Killham, University of Aberdeen

ENVIRONMENT AGENCY Environment Agency reports can be obtained from the R&D Dissemination Centre, WRC plc, Frankland Road, Blagrove, Swindon, Wiltshire, SN5 8YF, United Kingdom.	
Cost-Benefit Analysis for Remediation of Land Contamination To provide advice on assessing the costs and benefits of different remedial techniques when evaluating and selecting the most appropriate remedial strategy for a site.	Published in December 1999. R&D Technical Report P316.
Costs and Benefits Associated with Remediation of Contaminated Groundwater: A Review of the Issues. To review and provide guidance on the issues associated with the costs and benefits of remediating contaminated groundwater.	Published in December 1999. R&D Technical Report P278 (Review) R&D Technical Report P279 (Guidance)
Guidance on the Use of Digital Environmental Data To provide guidance on the nature and use of digital environmental data in GIS for improved land quality data management.	Published in March 2000. R&D Technical Report NC/06/32. Prepared in collaboration with the British Geological Survey.
Guidance for the Safe Development of Housing on Land Affected by Contamination To provide good practice advice in respect of remediation of land contamination and its return to beneficial use for the purposes of housing.	Published in June 2000. R&D Publication 66. Prepared in collaboration with the National House Building Council.
Risks of Contaminated Land to Buildings, Building Materials and Services. A Literature Review. To provide a literature review of information on the assessment and management of risks from land contamination to buildings.	Published in 2000. R&D Technical Report P331.
Survey of Remedial Techniques for Land Contamination in England and Wales.	Published in 2000. R&D Technical report P301
Assessing the Wider Environmental Value of Remediating Land Contamination: A Review. To review the international approach to assessing the wider environmental effect of different remedial strategies as part of a selection process	Published in 2000. R&D Technical Report P238.

Guidance on the Assessment and Monitoring of Natural Attenuation of Contaminants in Groundwater To provide guidance on the assessment and monitoring of natural attenuation of contaminants in groundwater.	Published in 2000. R&D Publication 95.
Development of Appropriate Soil Sampling Strategies for Land Contamination To develop guidance to assist the design of a site investigation strategy in accordance with the site conceptual model and the data requirements for risk estimation and evaluation.	Published in 2000. R&D Publication
Technical guidance for dealing with Special Sites	Published in 2001 R&D Publication
Bioremediation of contaminated soils with biomass fuel crops	
A review of remedial options for DNAPL source treatment To review the international experience of source treatment of DNAPL contaminants to evaluate information transfer and prioritisation of research into the UK.	Project completed (available shortly) R&D Technical Report P
Site for Innovative Research on Natural Attenuation (SIREN) To study the application of natural attenuation at a specific site and to encourage and disseminate the outcome of projects to benefit our wider understanding of the applicability and implementation of natural attenuation.	On-going project. R&D Publication
Guidance on monitoring and verification of remedial treatments for land contamination To provide guidance on the monitoring requirements and the verification of different remedial techniques to enable performance to be established during remediation and after works have been completed.	On-going project.
Case Study CBA	Ongoing

Development of Remedial Treatment Action Data Sheets	Ongoing First 5 data sheets on biological treatments will be available through the Agency's web site: www.environment-agency.gov.uk
Technical Training on inspection and remediation of contaminated land To produce a training package for those undertaking site inspections and/or remediation of contaminated soils and groundwater.	Ongoing
Landfill remediation technologies – potential use in the context of the landfill directive	New start in 2001/02
Guidance on Permeable Reactive Barriers	New start in 2001/02
Field study of the performance of cover systems for land remediation To provide baseline field evidence for the long term performance of cover systems to improve regulatory confidence in their appropriate application.	New start in 2001/02
SCOTLAND AND NORTHERN IRELAND FORUM FOR ENVIRONMENTAL RESEARCH (SNIFFER) Reports are available from the Foundation for Water Research, Allen House, The Listons, Liston Road, Marlow, Bucks SL7 1FD, UK.	
Protocol and Guidance Manual for Assessing Potential Adverse Effects of Substances on Designated Terrestrial Ecosystems To provide guidance on deriving site-specific assessment criteria for unacceptable risk to ecosystems.	Published in December 1999.
Framework for Deriving Numeric Targets to Minimise the Adverse Human Health Effects of Long-term Exposure to Contaminants in Soil To provide guidance on deriving site-specific assessment criteria for unacceptable chronic risk to human health.	Published in January 2000. Report No. SR99(02)F

CONSTRUCTION INDUSTRY RESEARCH AND INFORMATION ASSOCIATION (CIRIA)	
Remedial Engineering for Closed Landfill Sites. To provide guidance on the range of options for restoring closed landfill sites to a range of different end uses.	Funders Report CP/61. For information contact CIRIA at 6 Storey's Gate, Westminster, London, SW1P 3AU.
Remedial Processes for Contaminated Land: Principles and Practice. To provide good practice guidance on the selection and implementation of certain categories of process-based technologies.	Funders Report R000. For information contact CIRIA at 6 Storey's Gate, Westminster, London, SW1P 3AU.
Contaminated Land: Financial Control of Risk. To provide guidance to those involved in the redevelopment of brownfield sites on how to manage and limit the financial risk posed.	Funders Report. For information contact CIRIA at 6 Storey's Gate, Westminster, London, SW1P 3AU.
Contaminated land: in-house training material To produce training package aimed at the construction industry to raise awareness of the application of a range of remedial techniques and approaches to risk assessment.	On-going project.
Biological treatment for contaminated land: case studies. To develop good practice guidance when using biological treatments for remediating land contaminated in the UK.	On-going project.
Client's guide for building on brownfield sites. To provide guidance to the construction industry on adopting a sustainable approach to building on contaminated sites.	On-going project.
Safe working practice on contaminated land – training material. To provide training for those responsible for site safety and construction staff working on redevelopment of land affected by contamination.	New start in 2000/2001.

5. REFERENCES

1. Department of the Environment, Transport, and the Regions (2000) Environmental Protection Act 1990: Part IIA. Contaminated Land. Circular 02/2000. Available from the Stationery Office, PO Box 29, Norwich, NR3 1GN, United Kingdom: ISBN 0-11-753544-3 (Available on the web at www.environment.detr.gov.uk/contaminated/land/index.htm.)

2. Urban Task Force (1999) Towards an Urban Renaissance. Available from E & FN Spon Customer Service, International Thomson Publishing Services Ltd, Cheriton House, North Way, Andover, Hampshire, SP10 5BE, United Kingdom: ISBN 1-85112-165-X (An execu-tive summary is available on the web at www.regeneration.detr.gov.uk/utf/renais/index.htm.)

3. Environment Agency (2000)

4. DETR publication on research – check reference

UNITED STATES OF AMERICA

1. LEGAL AND ADMINISTRATIVE ISSUES

Three different federal programs provide the authority to respond to releases of hazardous substances that endanger public health or the environment: (1) In response to a growing concern about contaminated sites, Congress passed the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) in 1980. Commonly known as Superfund, the program under this law is the central focus of federal efforts to clean up releases of hazardous substances at abandoned or uncontrolled hazardous waste sites. The program is funded, in part, by a trust fund based on taxes on the manufacture of petroleum and other basic organic and inorganic chemicals. (2) The second program is directed at corrective action at currently operating hazardous waste management facilities. This program is authorized by the Resource Conservation and Recovery Act of 1980 (RCRA) and its subsequent amendments. RCRA corrective action sites tend to have the same general types of waste as Superfund sites. Environmental problems are generally less severe than at Superfund sites although numerous RCRA facilities have corrective action problems that could equal or exceed those of many Superfund sites. (3) The third program, also authorized by RCRA, is a comprehensive regulatory program for underground storage tanks (USTs) storing petroleum or certain hazardous substances. This law requires owners and operators of new tanks and tanks already in the ground to prevent, detect, and cleanup releases. As of March 2002, over 422,000 confirmed releases had been reported, over 387,000 cleanups initiated, and over 277,000 cleanups completed.

A. Implementation of Hazardous Waste Cleanup Legislation

Each program has a formal process for identifying, characterizing, and remediating contaminated sites. These processes generally involve joint implementation with state agencies and the involvement of various groups, such as local government agencies, local residents, businesses, and environmental public interest groups. Superfund is administered by EPA and the states under the authority of the CERCLA. Although the terminology may differ from one program to another, each follows a process more-or-less similar to this one. Thus, in addition to comprising a defined single program, activities in the Superfund program substantially influence the implementation of the other remediation programs.

RCRA assigns the responsibility for corrective action to facility owners and operators and authorizes EPA to oversee corrective action. Unlike Superfund, RCRA responsibility is delegated to states. As of September 2002, EPA has authorized 38 states and territories to implement the RCRA Corrective Action program.

The UST program is primarily implemented by states, whose UST requirements may be more stringent than federal regulations. The federal UST regulations require tank owners to monitor the status of their facilities and immediately report leaks or spills to the implementing agency. The federal regulations require UST owners and operators to respond to a release by: reporting the release; removing its source; mitigating fire and safety hazards; investigating the extent of contamination; and cleaning up soil and ground water as needed to protect human health and the environment.

B. Policy Developments

Ongoing cleanup programs are focusing on the productive reuse of properties and “Brownfields” or site reuse initiatives have become prominent at federal and state levels. Brownfields are abandoned, idled, or under-used industrial and commercial facilities where expansion or redevelopment is complicated by real or perceived environmental contamination. Estimates range from 450,000 to 600,000 such sites in the United States. A growing realization of their great potential has heightened interest in their cleanup and redevelopment. EPA has funded 437 Brownfield Assessment Pilots and 28 Showcase Communities projects to stimulate work in this area. The Assessment Pilots are funded at up to $200,000 to local communities to chart their own course toward revitalization. The pilots are seen as catalysts for change in local communities, and often spur community involvement in local land use decision-making. EPA has provided 143 Brownfields Cleanup Revolving Loan Fund grants for up to $1,000,000. In addition, EPA has provided Brownfields job training and development grants to 56 communities to provide environmental training for residents near brownfield sites. These programs have generated more than 15,000 jobs and returned about $2.50 of private investment for every public dollar spent.

These site reuse efforts were not originally envisioned when the Superfund and RCRA laws, under which they have been operated, were enacted. In January 2002, the President signed a new "Brownfields law, formally titled the "Small Business Liability Relief and Brownfields Revitalization Act," creating an opportunity to take further action at contaminated properties. The new law provides the needed capabilities to increase funding for assessment and cleanup, and to expand the scope of eligible parties and activities. The law responds directly to some of the biggest limitations of the earlier site reuse efforts -- providing new direct grants for cleanup, adding flexibility to cumbersome cleanup rules and including sites with petroleum contamination such as abandoned gas stations. The President's proposed 2003 budget requests $200 million for Brownfields – more than doubling the size of the current program.

The proposed funding increase will certainly expand the number of communities receiving help, but just as significant over the long run are the sweeping liability reforms in the bill. Clarifying Superfund liability provides increased certainty – the kind of certainty that communities and the private sector need to feel comfortable investing in site reuse projects. With specific provisions for innocent landowners, prospective purchasers and contiguous property owners – the bill generally protects owners and purchasers who did not contribute to the contamination, who conducted appropriate inquiry before the purchase and who exercised appropriate care for the property. The law will stimulate a new willingness to undertake site reuse projects because it removes the uncertainty of Superfund liability that clouded many potential redevelopment deals.

In addition to increasing funding and reforming liability, the law creates a strong, balanced relationship between the federal government and state and tribal programs. The law provides up to $50 million per year to support state and tribal response programs. The regulatory primacy of State programs is ensured by barring EPA from using Superfund enforcement authorities at sites cleaned up under a State response program. The Federal safety net is preserved through limited circumstances where EPA can be involved in a site and communities are further protected by requiring a public record of sites under State programs.

EPA is moving forward with a full-scale implementation effort involving states and tribes as partners and co-implementors. In addition, EPA is building on the Brownfields law to continue bringing reuse concepts into all programs dealing with contaminated properties, including Superfund, RCRA, UST and Federal facilities cleanup programs. For example, in the Superfund program the reuse of contaminated sites is a priority and areas that were once dangerous are now being cleaned up and turned into office parks, playing fields, industrial centers, shopping centers, residential areas, tourist centers, and wetlands. Beneficial use has started or is about to start at over 300 NPL sites. The commercial uses will support over 15,000 on-site jobs with over $500 million in annual incomes. There will also be over 60,000 acres of ecological and recreational uses. In addition, EPA has started a grant initiative to clean up and reuse sites with abandoned underground petroleum tanks. The program places special emphasis on environmental problems caused by the fuel additive MTBE (methyl tertiary butyl ether). The program entails competitively awarded grants of $100,000 to states for community pilot projects to plan cleanups, stop contamination of ground water, protect public health, and allow for future economic development of the sites. Ten grants were initially included and EPA has recently expanded the program with 40 additional grants.

2. IDENTIFICATION OF CONTAMINATED SITES

Almost half a million sites with potential contamination have been reported to state or federal authorities, based on a 1996 assessment. Regulatory authorities have identified most of the contaminated sites. Nevertheless, new ones continue to be reported each year, but at a declining rate. It is estimated that the cost of remediating sites from the 1996 assessment will be about $187 billion (in 1996 dollars), and that it will take at least several decades to completely cleanup all the identified sites.

3. TRENDS AND ANTICIPATED REMEDIAL TECHNOLOGY USE

As part of the quest for more efficient and cost-effective site remediation technologies, a few subject areas are particularly worthy of note at this time. These represent some of the focus areas in greatest need of new technology.

The presence of **DNAPLs** (dense non-aqueous phase liquids) is probably the single most important factor affecting our ability to attain clean-up levels in ground water. Studies have shown that pumping and treating will often not achieve cleanup goals in a reasonable time frame. In addition, the total costs to complete a groundwater cleanup are frequently not recognized either because of a 30 year planning horizon or as a result of discounting when considering the time value of money. Relatively little data are available for projects employing DNAPL treatment technologies, especially data documenting the long-term effects on ground water quality. There is interest in the potential for using in situ processes such as steam extraction, six-phase thermal heating, oxidation, surfactant-cosolvent flushing, and even biological processes. Oxidation is frequently used by a limited number of vendors at full-scale, primarily for petroleum contamination. Otherwise, with a few notable exceptions, there is relatively little field demonstration activity for either surfactant and co-solvent flushing or thermal vaporization and mobilization processes. This is an important shortcoming because DNAPLs are believed to be present at many sites. Future work is necessary to evaluate the capability of these treatment processes and to determine the result of partial source term removal on the resulting groundwater quality.

The trend toward greater use of in situ treatment processes has contributed to a need for **improved site characterization technologies**. In the past, site characterization primarily involved production of contaminant concentration profiles for the purpose of risk assessment. Now, however, with greater interest in situ processes, it is necessary to better understand subsurface conditions to assess the feasibility of in situ remediation options; to design these processes; to operate the in situ technologies with optimum feedback and process control; and to know when treatment may be stopped because acceptable residual levels have been achieved. There is a particular need to improve our ability to reliably locate DNAPL through direct or indirect methods. EPA is developing a Field Analytical Technologies Encyclopedia (FATE) at http://fate.cluin.org.

There is a growing awareness that better site data can improve decision-making at hazardous waste sites. These improvements can be achieved through use of an integrated approach that combines systematic planning, dynamic work plans, and real-time measurement technologies to plan and implement data collection. By carefully identifying and managing the potential causes of error (i.e., the sources of uncertainty) the capabilities of new **field-based characterization and monitoring** technologies can be realized. This has particular significance for Brownfields and voluntary cleanup programs where time and cost are a primary concern for the redevelopment and reuse of properties.

There is a strong interest in bringing more efficiency to remediation efforts through use of **optimization** techniques. The EPA, Corps of Engineers, Air Force, and other federal agencies have been working to identify and evaluate tools for optimizing pump-and-treat systems. These agencies are also developing programs to identify opportunities for realizing cost savings while maintaining acceptable levels of risk. Tools including mathematical optimization algorithms, geostatistical models, and comprehensive system audits have shown promising results for significantly improving performance and reducing operation and maintenance costs. EPA has recently completed a nationwide effort to optimize pump and treat systems financed by the Superfund Program using a process called Remediation System Evaluations (RSEs). The RSEs, similar to a system audit, identified a potential reduction in annual operating costs of 36% or nearly $5 million for the 20 evaluated sites and many opportunities to improve remedy protectiveness with respect to human health and the environment. EPA currently is considering expanding this effort to more Superfund sites and other EPA programs.

Monitored natural attenuation continues to receive attention as an alternative to pump-and-treat systems and as a final polishing step for various in situ remedies. Although natural attenuation offers significant advantages, there are some important uncertainties about attenuation rates and endpoints. EPA has issued a final guideline on this process that emphasizes the need for source control and rigorous long-term monitoring. Successful monitoring programs need to be demonstrated, perhaps using new sensor technology.

MTBE is a contaminant, which is being found with alarming frequency in groundwater supplies. MTBE is much more soluble and resistant to natural biodegradation than other gasoline constituents, such as benzene, toluene, ethylbenzene, and xylenes (BTEX). MTBE plumes are usually larger, leading to more drinking water wells being affected and more difficult and expensive cleanups. This constituent is more expensive to treat at both the wellhead and in situ because it is harder to strip and biodegrade. EPA has prepared 303 site profiles of drinking water and remediation sites that treat soil and ground water contaminated with MTBE. These studies are accessible through a web site (http://clu-in.org/products/mtbe), which has been established to help site managers assess technologies.

4. RESEARCH, DEVELOPMENT, AND DEMONSTRATION

Federal agencies currently are coordinating several technology development and commercialization programs. The Department of Energy (DOE) continues to lead in funding for the development new environmental cleanup technologies. These technologies are focused on improving the clean up at DOE sites and include processes such as bioremediation, electrokinetics, and biosorption of uranium.

The Department of Defense (DOD) has several technology research and development programs targeted at helping commercialize remediation technologies. The Environmental Security Technology Certification Program (ESTCP) is designed to promote the demonstration and validation of the most promising innovative technologies that target DOD's most urgent environmental needs. It is funded at $21 million in fiscal year (FY) 2002. The Strategic Environmental Research and Development Program (SERDP) is a joint program with DOD, DOE, and EPA, funded at $62.9 million in FY02, which devotes 36 percent of its resources to remediation and site characterization technologies. DOD's high priority cleanup technology needs include: unexploded ordinance (new sensors, signal processing and risk assessment); compliance (source determination, fate and transport, and aircraft noise); cleanup (remediation technologies for explosives in soil and ground water); pollution prevention (green munitions and green energetics); and conservation (range sustainability issues).

EPA's program for the evaluation of new cleanup technologies is the Superfund Innovative Technology Evaluation or SITE program. The SITE Demonstration Program encourages the development of innovative treatment technologies and new technologies for monitoring and measuring. In the Demonstration Program, technologies are field-tested on hazardous waste materials. Engineering and cost data are gathered so that potential users can assess applicability to a particular site. A similar program, which seeks to provide independent third-party verification of promising environmental technologies, is the Environmental Technology Verification (ETV) Program. The program operates 12 pilots covering a broad range of environmental areas. EPA partners with various public and private organizations in the different pilot areas to establish means for conducting the performance testing. Information for these programs is available from their web sites at http://www.epa.gov/ORD/SITE and http://www.epa.gov/etv. The publication source for EPA documents is http://www.epa.gov/ncepihom.

Cooperative public-private initiatives are particularly important because they focus on processes that private problem holders view as most promising for the future. The involvement of technology users helps to assure that the processes selected for development reflect actual needs and have a high potential for future application. Led by EPA, the Remediation Technologies Development Forum (RTDF) is a consortium of partners from industry, government, and academia, who share the common goal of developing more effective, less costly hazardous waste characterization and treatment technologies. RTDF achieves this goal by identifying high priority needs for remediation technology development.

EPA helps to develop partnerships between federal agencies (such as DOD and DOE) and private site owners (responsible parties, owners/operators) for the joint evaluation of remediation technologies. The program is organized around six action teams, which are co-chaired by a government and industry representative (Figure 1). Information is available from the RTDF home page at http://www.rtdf.org

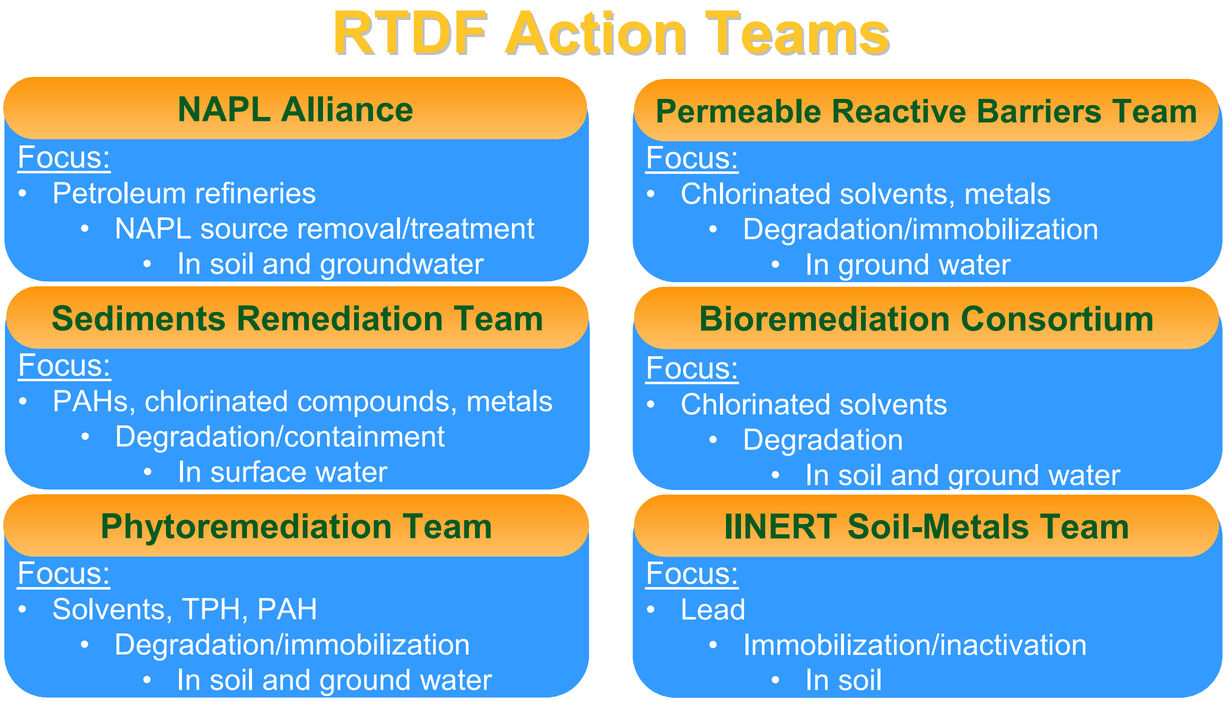
Agencies of the Federal Remediation Technologies Roundtable (including DOE, DOD and EPA) are involved in an ongoing effort to collect and distribute cleanup case studies of cost and performance data. The studies aid the selection and use of more cost-effective remedies by documenting experience from actual field applications. Recently, the Roundtable announced publication of 39 new studies of full-scale remediation and demonstration projects. This brings the total to 313 case studies, which are now available on the Roundtable's web site (http://www.frtr.gov) with a user-friendly search capability. Figure 2 indicates the types of contaminants and media addressed by the case studies. The federal agencies coordinated their individual documentation efforts by using standardized procedures to capture their cleanup experience. These procedures are contained in an Interagency Guide, which provides a recommended format for documenting cost, performance, and matrix and operational parameters for 29 specific technologies. By adopting a common reporting format, the federal agencies hope to increase the utility of data by making it easier to compare.

5. CONCLUSIONS

The new Brownfields law provides a significant new opportunity to cleanup and reuse contaminated properties. EPA will be providing funds to communities for assessment and cleanup assistance. In addition to the ongoing reuse efforts in the Superfund, RCRA, UST and Federal facilities cleanup programs, this should help to facilitate the emerging private site reuse market.

New technologies offer the potential to be more cost-effective than conventional approaches. *In situ* technologies, in particular, are in large demand because they are usually less expensive and more acceptable than above-ground options. Federal agencies and the private sector are actively involved in developing and demonstrating new treatment and site characterization technologies. Various forms of partnering are instrumental in increasing the efficiency and effectiveness of these efforts.

Figure 1: The six RTDF Action Teams



RTDF Action Teams

NAPL Alliance

Focus:
- Petroleum refineries
  - NAPL source removal/treatment
    - In soil and groundwater

Permeable Reactive Barriers Team

Focus:
- Chlorinated solvents, metals
  - Degradation/immobilization
    - In ground water

Sediments Remediation Team

Focus:
- PAHs, chlorinated compounds, metals
  - Degradation/containment
    - In surface water

Bioremediation Consortium

Focus:
- Chlorinated solvents
  - Degradation
    - In soil and ground water

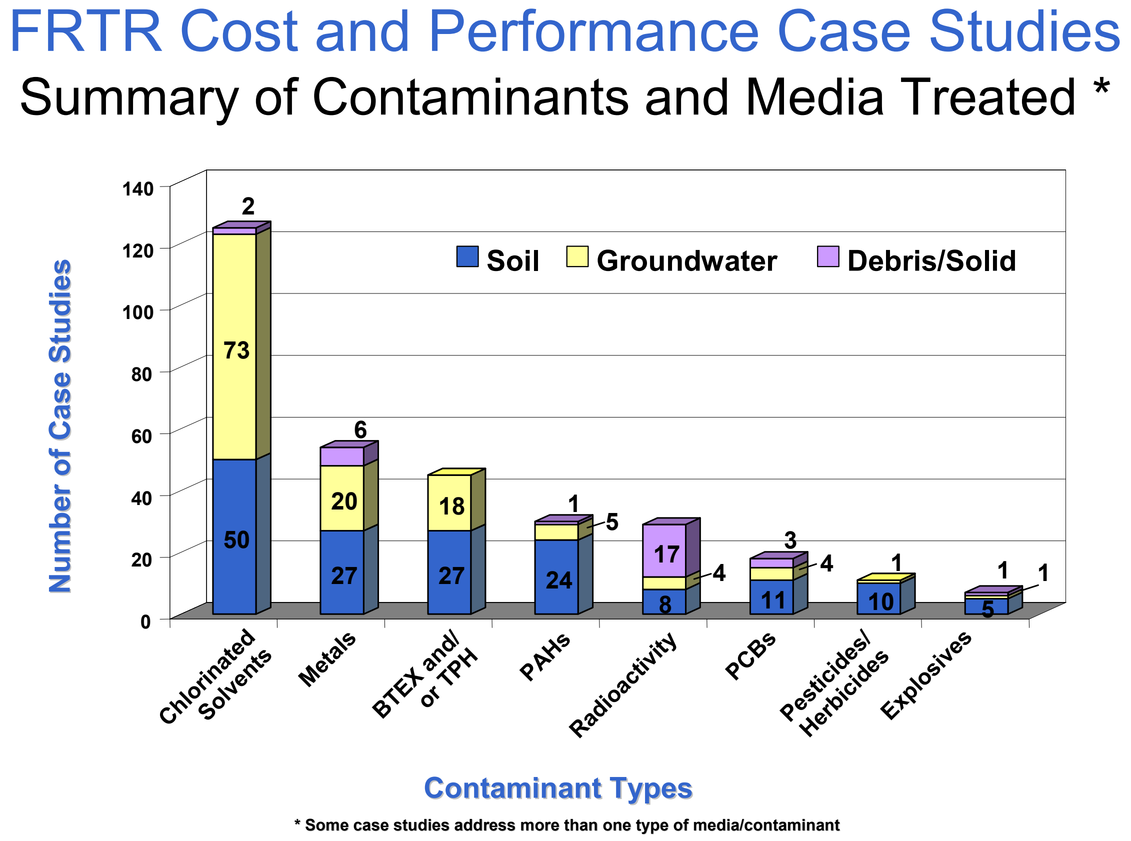
Phytoremediation Team

Focus:
- Solvents, TPH, PAH
  - Degradation/immobilization
    - In soil and ground water

IINERT Soil-Metals Team

Focus:
- Lead
  - Immobilization/inactivation
    - In soil

Figure 2: Types of contaminants and media addressed by case studies



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PILOT STUDY MISSION
October 1997
PHASE III — Continuation of NATO/CCMS Pilot Study: Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater

1. BACKGROUND TO PROPOSED STUDY

The problems of contamination resulting from inappropriate handling of wastes, including accidental releases, are faced to some extent by all countries. The need for cost-effective technologies to apply to these problems has resulted in the application of new/innovative technologies and/or new applications of existing technologies. In many countries, there is increasingly a need to justify specific projects and explain their broad benefits given the priorities for limited environmental budgets. Thus, the environmental merit and associated cost-effectiveness of the proposed solution will be important in the technology selection decision.

Building a knowledge base so that innovative and emerging technologies are identified is the impetus for the NATO/CCMS Pilot Study on "Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater (Phase II)." Under this current study, new technologies being developed, demonstrated, and evaluated in the field are discussed. This allows each of the participating countries to have access to an inventory of applications of individual technologies, which allows each country to target scarce internal resources at unmet needs for technology development. The technologies include biological, chemical, physical, containment, solidification/stabilization, and thermal technologies for both soil and groundwater. This current (Phase II) pilot study draws from an extremely broad representation and the follow up would work to expand this.

The current pilot study examined over fifty environmental projects. There were nine fellowships awarded to the study. A team of pilot study country representatives and fellows is currently preparing an extensive report of the pilot study activities. Numerous presentations and publications reported about the pilot study activities over the five-year period. In addition to participation from NATO countries, NACC and other European and Asian-Pacific countries participated. This diverse group promoted an excellent atmosphere for technology exchange. An extension of the pilot study will provide a platform for continued discussions in this environmentally challenging arena.

2. PURPOSE AND OBJECTIVES

The United States proposes a follow-up (Phase III) study to the existing NATO/CCMS study titled "Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater." The focus of Phase III would be the technical approaches for addressing the treatment of contaminated land and groundwater. This phase would draw on the information presented under the prior studies and the expertise of the participants from all countries. The output would be summary documents addressing cleanup problems and the array of currently available and newly emerging technical solutions. The Phase III study would be technologically orientated and would continue to address technologies. Issues of sustainability, environmental merit, and cost-effectiveness would be enthusiastically addressed. Principles of sustainability address the use of our natural resources. Site remediation addresses the management of our land and water resources. Sustainable development addresses the reuse of contaminated land instead of the utilization of new land. This appeals to a wide range of interests because it combines economic development and environmental protection into a single system. 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. International technology verification is another issue that will enable technology users to be assured of minimal technology performance. This is another important issue concerning use of innovative technologies. This Phase III study would have the following goals:

a) In-depth discussions about specific types of contaminated land problems (successes and failures) and the suggested technical solutions from each country's perspective,

b) Examination of selection criteria for treatment and cleanup technologies for individual projects,

c) Expand mechanisms and channels for technology information transfer, such as the NATO/CCMS Environmental Clearinghouse System,

d) Examination/identification of innovative technologies,

e) Examining the sustainable use of remedial technologies─looking at the broad environmental significance of the project, thus the environmental merit and appropriateness of the individual project.

3. DURATION

November 1997 to May 2002 for meetings.
Completion of final report: January 2003.

4. SCOPE OF WORK

First, the Phase III study would enable participating countries to continue to present and exchange technical information on demonstrated technologies for the cleanup of contaminated land and groundwater. During the Phase II study, these technical information exchanges benefited both the countries themselves and technology developers from various countries. This technology information exchange and assistance to technology developers would therefore continue. Emphasis would be on making the pilot study information available. Use of existing environmental data systems such as the NATO/CCMS Environmental Clearinghouse System will be pursued. The study would also pursue the development of linkages to other international initiatives on contaminated land remediation.

As in the Phase II study, projects would be presented for consideration and, if accepted by other countries, they would be discussed at the meetings and later documented. Currently, various countries support development of hazardous waste treatment/cleanup technologies by governmental assistance and private funds. This part of the study would report on and exchange information of ongoing work in the development of new technologies in this area. As with the current study, projects would be presented for consideration and if accepted, fully discussed at the meetings. Individual countries can bring experts to report on projects that they are conducting. A final report would be prepared on each project or category of projects (such as thermal, biological, containment, etc.) and compiled as the final study report.

Third, the Phase III study would identify specific contaminated land problems and examine these problems in depth. The pilot study members would put forth specific problems, which would be addressed in depth by the pilot study members at the meetings. Thus, a country could present a specific problem such as contamination at an electronics manufacturing facility, agricultural production, organic chemical facility, manufactured gas plant, etc. Solutions and technology selection criteria to address these problems would be developed based on the collaboration of international experts. These discussions would be extremely beneficial for the newly industrializing countries facing cleanup issues related to privatization as well as developing countries. Discussions should also focus on the implementation of incorrect solutions for specific projects. The documentation of these failures and the technical understanding of why the project failed will be beneficial for those with similar problems. Sustainability, environmental merit, and cost-benefit aspects would equally be addressed.

Finally, specific area themes for each meeting could be developed. These topics could be addressed in one-day workshops as part of the CCMS meeting. These topic areas would be selected and developed by the pilot study participants prior to the meetings. These areas would be excellent venues for expert speakers and would encourage excellent interchange of ideas.

5. NON-NATO PARTICIPATION

It is proposed that non-NATO countries be invited to participate or be observers at this NATO/CCMS Pilot Study. Proposed countries may be Brazil, Japan, and those from Central and Eastern Europe. It is proposed that the non-NATO countries (Austria, Australia, Sweden, Switzerland, New Zealand, Hungary, Slovenia, Russian Federation, *etc.*) participating in Phase II be extended for participation in Phase III of the pilot study. Continued involvement of Cooperation Partner countries will be pursued.

6. REQUEST FOR PILOT STUDY ESTABLISHMENT

It is requested of the Committee on the Challenges of Modern Society that they approve the establishment of the Phase III Continuation of the Pilot Study on the Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater.

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Lead Organization: U.S. Environmental Protection Agency

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Co-Partner Countries: Australia, Austria, Belgium, Canada, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Ireland, Japan, New Zealand, Norway, Poland, Portugal, Slovenia, Sweden, Switzerland, The Netherlands, Turkey, United Kingdom, United States

Addenda

Phase III Meetings Held: February 23-27, 1998, in Vienna, Austria
May 9-14, 1999, in Angers, France
June 26-30, 2000, in Wiesbaden, Germany
September 9-14, 2001, in Liège, Belgium
May 5-10, 2002, Rome, Italy