# NATO/CCMS Pilot Study 

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

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

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## NOTICE

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## CONTENTS

Introduction ..... 1
Projects Included in the NATO/CCMS Phase III Pilot Study ..... 3
Summary Table ..... 4
Project 1 Bioremediation of Oil-Polluted Loamy Soil ..... 7
Project 2: Pilot Test on Decontamination of Mercury-Polluted Soil ..... 16
Project 3: Permeable Treatment Beds ..... 20
Project 4 : Rehabilitation of Land Contaminated by Heavy Metals ..... 24
Project 5: Application of Bioscreens and Bioreactive Zones ..... 30
Project 6: Rehabilitation of a Site Contaminated by PAH Using Bio-Slurry Technique ..... 35
Project 7: Risk Assessment for a Diesel-Fuel Contaminated Aquifer Based on Mass Flow Analysis During Site Remediation ..... 37
Project 8: Obstruction of Expansion of a Heavy Metal/Radionuclide Plume Around a Contaminated Site by Means of Natural Barriers Composed of Sorbent Layers ..... 42
Project 9: Solidification/Stabilization of Hazardous wastes ..... 47
Project 10: Metal-Biofilm Interactions in Sulphate-Reducing Bacterial Systems ..... 54
Project 11: Predicting the Potential for Natural Attenuation of Organic Contaminants in Groundwater ..... 60
Project 12: Treatability Test for Enhanced In Situ Anaerobic Dechlorination ..... 65
Project 13: Permeable Reactive Barriers for In Situ Treatment of Chlorinated Solvents ..... 71
Project 14: Thermal Cleanup Using Dynamic Underground Stripping and Hydrous Pyrolysis/ Oxidation ..... 75
Project 15: Phytoremediation of Chlorinated Solvents ..... 83
Project 16: In-Situ Heavy Metal Bioprecipitation ..... 94
Project 17: GERBER Site ..... 99
Project 18: SAFIRA ..... 101
Project 19: Succesive Extraction-Decontamination of Leather Tanning Waste Deposited Soil ..... 104
Project 20: Interagency DNAPL Consortium Side-by-Side Technology Demonstrations at Cape Canaveral, Florida ..... 106
Project 21: Development and Use of a Permeable Adsorptive Reactive Barrier System for Ground Water Clean-up at a Chromium Contaminated Site ..... 110
Project 22: Thermal In-Situ Using Steam Injection ..... 113
Project 23: Bioremediation of Pesticides ..... 116
Project 24: Surfactant-Enhanced Aquifer Remediation ..... 119
Project 25: Liquid Nitrogen Enhanced Remediation (LINER): A New Concept for the Stimulation of the Biological Degradation of Chlorinated Solvents ..... 123
Project 26: SIREN: Site for Innovative Research on Monitored Natural Attenuation ..... 126
Project 27: Hydro-Biological Controls on Transport and Remediation of Organic Pollutants for Contaminated Land ..... 130
Project 28: Demonstration of a Jet Washing System for Remediation of Contaminated Land ..... 133
Project 29: Automatic Data Acquisition and Monitoring System for Management of Polluted Sites ..... 135
Country Tour De Table Presentations ..... 138
Armenia ..... 139
Austria ..... 144
Belgium ..... 146
Canada ..... 150
Czech Republic ..... 153
Finland. ..... 158
France ..... 159
Germany ..... 161
Greece ..... 166
Italy ..... 168
Japan. ..... 173
Lithuania ..... 179
The Netherlands ..... 184
Norway ..... 190
Slovenia ..... 191
Switzerland ..... 217
Turkey. ..... 220
United Kingdom ..... 223
United States of America ..... 230
Country Representatives ..... 235
Attendees List ..... 238
Pilot Study Mission ..... 246

## 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 second meeting of the Phase III Pilot Study on the Evaluation of Demonstrated and Emerging Technologies for the Treatment and Clean Up of Contaminated Land and Groundwater. The United States is the lead country for the Pilot Study, and Germany and The Netherlands are the Co-Pilot countries. The first phase 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 focuses on the technologies for treating contaminated land and groundwater. This Phase is addressing issues of sustainability, environmental merit, and cost-effectiveness, in addition to continued emphasis on emerging remediation technologies. The objectives of the study are to critically evaluate technologies, promote the appropriate use of technologies, use information technology systems to disseminate the products, and to foster innovative thinking in the area of contaminated land. The Phase III Mission Statement is provided at the end of this report.

The first meeting of the Phase III study was held in Vienna, Austria, on February 23-27, 1998. The meeting included a special technical session on treatment walls and permeable reactive barriers. The proceedings of the meeting and of the special technical session were published in May 1998. The second meeting of the Phase III Pilot Study convened in Angers, France, on May 9-14, 1999, with representatives of 18 countries attending. A special technical session on monitored natural attenuation was held. This report and the general proceedings of the 1999 annual meeting were published in October 1999. This third meeting was held in Wiesbaden, Germany from June 26-30, 2000. The special technical session focused on decision support tools.

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<br>Walter W. Kovalick, Jr., Ph.D.<br>Co-Directors

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## SUMMARY TABLE

|  |  | MEDIUM |  | CONTAMINANT |  |  |  |  | NOTES | mU000 |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| PROJECT | COUNTRY | ¢ $\overline{\text { ¢ }}$ |  | O8 | $\begin{aligned} & \text { di } \\ & \text { On } \end{aligned}$ |  | 옴 | - |  |  |  |
| 1. Bioremediation of Oil-Polluted Loamy Soil | Belgium | $\checkmark$ |  |  | $\checkmark$ |  | $\checkmark$ |  | PAHs, munitions chemicals |  |  |
| 2. Pilot Test on Decontamination of Mercury-Polluted Soil | Czech Rep. | $\checkmark$ | $\checkmark$ |  | $\checkmark$ |  |  | $\checkmark$ | Hg , metals, PAHs, TPH | $\checkmark$ |  |
| 3. Permeable Treatment Beds | Germany |  | $\checkmark$ | $\checkmark$ | $\checkmark$ |  | $\checkmark$ | $\checkmark$ | PAHs, BTEX, TCE, PCE |  |  |
| 4. Rehabilitation of Land Contaminated by Heavy Metals | Greece | $\checkmark$ |  |  |  |  |  | $\checkmark$ | $\mathrm{Pb}, \mathrm{Zn}, \mathrm{Cd}, \mathrm{As}, \mathrm{H}^{+}$, $\mathrm{SO}_{4}=$ |  |  |
| 5. Application of BioScreens and Bioreactive Zones | Netherlands |  | $\checkmark$ | $\checkmark$ | $\checkmark$ | $\checkmark$ | $\checkmark$ |  | Chlorinated pesticides, BTEX, TPH, HCH, PCE, TCE | $\checkmark$ |  |
| 6. Rehabilitation of a Site Contaminated by PAH Using Bio-Slurry Technique | Sweden | $\checkmark$ |  |  | $\checkmark$ |  |  | $\checkmark$ | PAHs, cyanides, metals, ammonium compounds |  |  |
| 7. Risk Assessment for a Diesel-Fuel Contaminated Aquifer Based on Mass Flow Analysis During Site Remediation | Switzerland |  | $\checkmark$ |  |  |  | $\checkmark$ |  | PHC | $\checkmark$ |  |
| 8. Obstruction of Expansion of a Heavy Metal/Radionuclide Plume Around a Contaminated Site by Means of Natural Barriers Composed of Sorbent Layers | Turkey | $\checkmark$ | $\checkmark$ |  |  |  |  | $\checkmark$ | $\mathrm{Pb}, \mathrm{As}, \mathrm{Cr}, \mathrm{Cu}, \mathrm{Cd}$, $\mathrm{Hg}, \mathrm{Ni}, \mathrm{Zn} ;{ }^{137} \mathrm{Cs},{ }^{90} \mathrm{Sr}$, 238 U |  |  |
| 9. Solidification/Stabilization of Hazardous Wastes | Turkey | $\checkmark$ |  |  | $\checkmark$ | $\checkmark$ |  | $\checkmark$ | PCBs, AOX, metals |  |  |
| 10. Metal-Biofilms Interactions in Sulfate-Reducing Bacterial Systems | UK |  | $\checkmark$ |  |  |  |  | $\checkmark$ | Metals ( $\mathrm{Cu}, \mathrm{Zn}, \mathrm{Cd}$ ), radionuclides (Labscale) | $\checkmark$ |  |
| 11. Predicting the Potential for Natural Attenuation of Organic Contaminants in Groundwater | UK |  | $\checkmark$ | $\checkmark$ | $\checkmark$ |  | $\checkmark$ | $\checkmark$ | Coal tars, phenols, creosol, xylenols, BTEX, $\mathrm{NH}_{4}{ }^{+}$ | $\checkmark$ |  |
| 12. Treatability Test for Enhanced In Situ Anaerobic Dechlorination | USA |  | $\checkmark$ | $\checkmark$ | $\checkmark$ |  |  |  | TCE, DCE, VC, PCE |  |  |
| 13. Permeable Reactive Barriers for In Situ Treatment of Chlorinated Solvents | USA |  | $\checkmark$ | $\checkmark$ |  |  |  | $\checkmark$ | PCE, TCE, DCE | $\checkmark$ |  |
| 14. Thermal Cleanup Using Dynamic Underground Stripping and Hydrous Pyrolysis/Oxidation | USA | $\checkmark$ | $\checkmark$ | $\checkmark$ |  | $\checkmark$ |  |  | PAHs, fuels, gasoline chlorinated solvents, pentachlorophenol | , |  |


|  |  | MEDIUM |  | CONTAMINANT |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| PROJECT | COUNTRY | $\overline{\bar{\circ}}$ |  | $\begin{aligned} & \text { © } \\ & \hline \end{aligned}$ | $\begin{aligned} & \text { © } \\ & \text { む } \end{aligned}$ |  | 옴 |  | NOTES | m 4 4 0 0 |
| 15. Phytoremediation of Chlorinated Solvents | USA |  | $\checkmark$ | $\checkmark$ |  |  |  |  | TCE, TCA, DCE, PCE, xylenes, methyl chloride, TMB | $\checkmark$ |
| 16. In-Situ Heavy Metal Bioprecipitation | Belgium |  | $\checkmark$ |  |  |  |  | $\checkmark$ | Heavy Metals (Zn, Cd $\mathrm{As}, \mathrm{Pb}, \mathrm{Cr}, \mathrm{Ni}, \mathrm{Cu}$, sulfate) |  |
| 17. GERBER Site | France | $\checkmark$ | $\checkmark$ | $\checkmark$ | $\checkmark$ | $\checkmark$ |  | $\checkmark$ | Chlorinated solvents, BTEX, PCBs, phenols, phthalates, $\mathrm{Pb}, \mathrm{Zn}$ |  |
| 18. SAFIRA | Germany |  | $\checkmark$ | $\checkmark$ |  |  |  |  | Complex contamination, chlorobenzene |  |
| 19. Successive Extraction Decontamination of Leather Tanning Waste Deposited Soil | Turkey |  |  | $\checkmark$ |  |  |  | $\checkmark$ | Tanning wastes |  |
| 20. Interagency DNAPL Consortium Side-by-Side Technology Demonstrations at Cape Canaveral, Florida | USA | $\checkmark$ | $\checkmark$ |  |  |  |  |  | DNAPLs |  |
| 21. Development and Use of a Permeable Adsorptive Reactive Barrier System for Ground Water Clean-up at a Chromium-Contaminated Site | Switzerland |  | $\checkmark$ |  |  |  |  | $\checkmark$ | Chromium (VI) |  |
| 22. Thermal In-Situ Using Steam Injection | Germany | $\checkmark$ |  | $\checkmark$ |  |  |  |  | TCE, BTEX |  |
| 23. Bioremediation of Pesticides | USA | $\checkmark$ |  |  |  | $\checkmark$ |  |  | Chlordane, DDT, DDD, DDE, dieldrin, molinate, toxaphene |  |
| 24. Surfactant-Enhanced Aquifer Remediation | USA |  | $\checkmark$ | $\checkmark$ |  |  |  |  | PCE |  |
| 25. Liquid Nitrogen Enhanced Remediation (LINER) | Netherlands |  | $\checkmark$ | $\checkmark$ |  |  |  |  | Chlorinated hydrocarbons |  |
| 26. SIREN: Site for Innovative Research on Monitored Natural Attenuation | UK |  | $\checkmark$ | $\checkmark$ |  |  |  |  | Organic solvents |  |
| 27. Hydro-Biological Controls on Transport and Remediation of Organic Pollutants for Contaminated Land | UK | $\checkmark$ | $\checkmark$ | $\checkmark$ | $\checkmark$ |  |  |  | PAHs, phenols, substituted benzenes |  |
| 28. Demonstration of a Jet Washing System for Remediation of Contaminated Land | UK | $\checkmark$ |  |  |  |  | $\checkmark$ |  | Tars, petroleum hydrocarbons |  |
| 29. Automatic Data Acquisition and Monitoring System for Management of Polluted Sites | Italy | $\checkmark$ | $\checkmark$ | $\checkmark$ |  |  |  |  | TPH, BTEX |  |

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
$\mathrm{VC}=$ vinyl chloride
VOCs = volatile organic compounds

| Project No. 1 |  |  |
| :--- | :--- | :--- | :--- |
| Bioremediation of Oil-Polluted Loamy Soil |  |  |

Please note that this project summary was not updated since the 1999 report. An update will be provided in the 2001 report.

## 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 reconnoitoring soil examination, at $3.500 \mathrm{~m}^{3}$. 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)

|  | $>525 m g / k g$ DES | $>1000 \mathrm{mg} / \mathrm{kg}$ DS | $>5000 \mathrm{mg} / \mathrm{kg}$ DS |
| :--- | :--- | :--- | :--- |
| Depth $(\mathbf{c m})$ |  |  |  |
| $\mathbf{0 - 2 0 0}$ | $9231 \mathrm{~m}^{3}$ | $6284 \mathrm{~m}^{3}$ | $943 \mathrm{~m}^{3}$ |
|  | 14,770 tons | 10,054 tons | 1509 tons |
| $\mathbf{0 - 2 5 0}$ | $10,997 \mathrm{~m}^{3}$ | $6997 \mathrm{~m}^{3}$ | $1050 \mathrm{~m}^{3}$ |
|  | 17,995 tons | 11,196 tons | 1680 tons |
| $\mathbf{0 - 3 0 0}$ | $12,763 \mathrm{~m}^{3}$ | $7711 \mathrm{~m}^{3}$ | $1156 \mathrm{~m}^{3}$ |
|  | 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 $>5000 \mathrm{mg} / \mathrm{kg}$ 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:

- $\quad$ 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.

- $\quad$ 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 1000 mgkg 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:

- characterisation 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 $\mathrm{C} / \mathrm{N}$ 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 $\left(\mathrm{CO}_{2}\right.$ 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 $\mathrm{CO}_{2}$ 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 $\mathrm{CO}_{2}$ 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 $50 \mathrm{~m}^{3}$. 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


Figure 2


Figure 3



Figure 4


FIG.4: DISPERTION OF HYDROCARBONS AFTER 5 MONTHS OF BIOREMEDIATION
Ecorem (concentration of hydrocarbons in in $\mathrm{mg} / \mathrm{kg} \mathrm{DM}$ )

Figure 5


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

Ecorem
$039 \quad$ F-1005-M0
Figure 6


Figure 7

FIG.7: IMPRESSION OF THE FUTURE SOIL REMEDIATION CENTER ECorem

| Project No. 2 |  |  |  |
| :---: | :---: | :---: | :---: |
| Pilot Test on Decontamination of Mercury-Polluted Soil |  |  |  |
| Location <br> Spolchemie a.s., Ústí nad Labem, Czech Republic | Project Status Final report | Contaminants Metallic mercury | Technology Type Wet gravity separation |
| Technical Contact Marek Stanzel KAP, Ltd. <br> Trojská 92 <br> 17100 Prague 7 <br> Czech Republic <br> www.kap.cz | Project Dates <br> Accepted 1999 <br> Final Report 2000 | Media <br> Soil |  |
| Tel: (00-420-2) 83090614 <br> Fax: (00-420-2) 83090658 <br> E-mail: <br> m.stanzel@prg.kap.cz | Costs Documented? Yes | Project Size <br> Pilot test $-1 \mathrm{~m}^{3}$ (2 tons) | Results Available? No |

## 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 $222.740 \mathrm{~m}^{3}$ 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 $\mathrm{m}^{3}$ 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 $120,000 \mathrm{ppm}$ 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 ( $<0.003 \mathrm{mg} / \mathrm{l}$ ) 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 $100,000 \mathrm{ppm}$. 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 $(<0.003 \mathrm{mg} / \mathrm{l})$.

## 8. COSTS

The total project cost was $0.5 \mathrm{M} \mathrm{CZK}(13,000 \mathrm{USD})$. 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.

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| Project No. 3 |  |  |
| :---: | :---: | :---: |
| Permeable Treatment Beds |  |  |
| Technical Contact: | Location: <br> Former solvent blending plant, Essen, Germany | Project Status: Interim Report, Field tests finalized |
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| Media: <br> Groundwater | Technology Type: | Project Dates: <br> Accepted 1997 |
|  | Permeable reactive barrier as in- |  |
|  | situ groundwater remediation |  |
| No. Cost estimation is available. | Chlorinated and nonchlorinated | Full-scale |
|  | solvents, BTEX-aromates, TCE, |  |
|  |  |  |
| Results available? <br> No. Field test results available. |  |  |
|  |  |  |  |  |

Please note that this project summary was not updated since the 1999 report. An update will be provided in the 2001 report.

## 1. INTRODUCTION

A pilot groundwater treatment plant was installed at a former industrial site in Essen, Germany, where organic solvents had been stored and processed in a small chemical plant for several decades. Leakage and handling losses caused significant soil and groundwater contamination, mainly by BTEX and CHC. The contaminated aquifer has low hydraulic conductivity and is only 2-3 m thick. The aquifer is covered by $4-11 \mathrm{~m}$ of thick, silty and clayey covering layers (loess). During investigations and conceptual remediation design, it was determined that the site was suitable to install adsorbent walls since conventional remediation and contamination control measures cannot be applied in a cost-efficient manner.

Subsequently, WCI and IWS studied and reported on various technical variants to install an adsorbent wall in a feasibility study. The study also established which data were necessary to arrive at the dimensions of the adsorbent wall. The feasibility study recommended that pilot tests be conducted on the site for this purpose.
The objective of the pilot tests was to obtain precise information on the adsorption potential for the contaminants at the site, the type and quantity of the required adsorbent material, the functioning of filters at different flow speeds, and the long-term effectiveness and attendant risks, if any, of installing an adsorbent wall.

Conducting the pilot tests involved the following principal tasks:

- Selecting a suitable adsorbent for the tests depending on water quality and the relevant contaminant concentrations at the site;
- Structural design and planning of the pilot plant;
- Operating and taking samples from the pilot plant, as well as carrying out laboratory analyses;
- Assessment of the pilot tests.


## 2. BACKGROUND/SITE DESCRIPTION

From 1952 to 1985, a chemical factory was located on an area of about $10,000 \mathrm{~m}^{2}$ in a city in the Ruhr area. Mostly solvents, like hydrocarbons, volatile chlorinated hydrocarbons, PAHs, petroleum, turpentine 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 $\left(\mathrm{k}_{\mathrm{f}}=6.6 \cdot 10^{-6} \mathrm{~m} / \mathrm{s}\right)$. The concentrations of main contaminants in groundwater are petrol hydrocarbons $23.6 \mathrm{mg} / 1$ to $164.0 \mathrm{mg} / \mathrm{l}$, volatile chlorinated hydrocarbons $27.0 \mathrm{mg} / \mathrm{l}$ and aromatic hydrocarbons $153.0 \mathrm{mg} / \mathrm{l}$. Furthermore, higher concentrations of manganese and iron are present.

The project is funded by the city of Essen and the state; Nordrhein-Westfalen, the former owner, went bankrupt.

## 3. DESCRIPTION OF THE PROCESS

The pilot plant was fed with groundwater, which was pumped directly from the aquifer into the front column. Two dosing pumps located behind a gravel bed in the front column fed groundwater into columns 1 and 2. The gravel filter served to hold back sediments as well as to eliminate iron and manganese.

- Column 1 contained:
- $\quad 45 \mathrm{~cm}$ gravel filter (size: 2 to 3.15 mm )
- $\quad 5 \mathrm{~cm}$ activated carbon ROW 0.08 supra
- $\quad 5 \mathrm{~cm}$ gravel filter (gravel size: 2 to 3.15 mm )
- $\quad 65 \mathrm{~cm}$ activated carbon ROW 0.08 supra

The thickness of the activated carbon bed in Column 1 corresponded to the recommended thickness of the activated carbon bed of the adsorbent wall in the feasibility study.

- Column 2 contained:
- $\quad 100 \mathrm{~cm}$ activated carbon ROW 0.08 supra

The treated water was led via an overflow into a trough located outside the container.
Groundwater analyses were based on the contamination at the site; their scope was determined by the feasibility study to install an adsorbent wall. The analyses covered field parameters, general parameters and parameters to quantify BTEX and volatile CHC contamination.
The analyzed general parameters included sum parameters for organic compounds as well as the parameters iron and manganese. A sum parameter for organic compounds was used in order to study whether it could serve as a substitute for analyses of individual substances. Moreover, the sum parameters were also used to check whether the results of individual analyses were plausible. Iron and manganese contents were determined in order to check whether precipitation of these substances would block the adsorbent wall.

Separate analyses were carried out for BTEX and volatile CHC. The number of analyzed parameters (16) was deliberately large so as to also cover important decomposition products such as vinyl chloride. Contaminant retention by the activated carbon was determined in two ways. First, contaminant concentrations were continuously monitored at the inlet, in the columns, and at the column outlets.

Secondly, following the conclusion of tests, the columns were disassembled and individual partitions of carbon samples were analyzed for contaminant content. Tests were carried out to determine whether iron and manganese precipitation or microbial activity in the activated carbon could block the adsorbent wall.

Water samples collected on 11 days were tested for numerous parameters; on the whole, over 1,600 individual results were obtained for water samples taken during pilot operation. The determined concentrations for dissolved organic carbons (DOC) ranged between 80 and $160 \mathrm{mg} / \mathrm{l}$ at the inlet. The DOC values correlate well with the CSB and TOC concentrations. No contaminant breakthrough was detected in samples from the outlets of the two columns over a period of almost half a year.

The pilot tests with Columns 1 and 2 confirm that putting up an adsorbent wall is feasible. With respect to contaminant retention, results of the pilot tests indicate that the long-term effectiveness would be much higher than the estimated period of 30 years in the feasibility study.

## 4. RESULTS AND EVALUATION

The pilot tests confirm the findings of the feasibility study, to the effect that the site is suited to put up an adsorbent wall. The following statements can be made with respect to the present tests:

- The pilot tests show good contaminant retention in the activated carbon, in fact much higher than what was assessed in the feasibility study. Contaminant breakthrough for toluene and trichloroethylene was determined at sampling point S2P50 (i.e., after flow through 50 cm ), Column 2, only at the end of the 5-month pilot test operation. By this time, throughput had reached 600 times the bed volume.
- The pilot tests indicate that the durability of the wall given a 70 cm -thick activated carbon layer would be much higher than the 30 years estimated in the feasibility study. The thickness of the carbon layer should therefore be reduced when the wall is put up.
- The DOC concentrations established during the pilot tests can almost entirely be traced to the contaminants detected at the site. It is therefore to be expected that the adsorbing potential of the activated carbon will not be impaired by natural organic compounds, such as humin.
- Data pertaining to the contaminant breakthrough suggest that the depletion of the adsorbing capacity of the activated carbon is accompanied by a sharp peak in the concentration of volatile substances. A suitable monitoring system should therefore be set up when the adsorbent wall is erected.
- The fact that the activated carbon could be regenerated after disassembling the plant suggests economic operation of the adsorbent wall.
- Laboratory analyses of the water and activated carbon samples indicate that iron and manganese precipitation will be insignificant and will not block the adsorbent wall.
- Microbial activity could not be detected in the gravel filter or in the activated carbon; it may be concluded that under the given site conditions, the build-up of bacterial film does not pose a risk.
- Preliminary laboratory tests to determine the choice of activated carbon as well as pilot tests must be carried out in all cases prior to setting up an adsorbent wall given the variance in site conditions.


## 5. COSTS

The costs for conducting the field tests have been EURO 50.000,--. The overall costs to erect the wall system and then fill it with activated carbon are estimated to be EURO 750.000,--. Included are additional costs for monitoring the water quality for 30 years, which is as 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.

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| Project No. 4 Rehabilitation of Land Contaminated by Heavy Metals |  |  |  |  |
| :--- | :--- | :--- | :--- | :---: |

## 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 characterised as toxic and 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 that migrate from the wastes. The project aims at developing (a) innovative, costeffective, 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 under development include:

## Preventive

- Application of alkaline additives to prevent acid generation from sulphidic wastes.
- Formation of surface barriers with bentonite, zeolite, or other additives to prevent pollutant migration from the pyrite cinders and calamina residues.
- Chemical stabilisation 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 sulphidic 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 sulphide mine <br> (argentiferous, galena, sphalerite, pyrite) | Sulphidic and oxidic <br> tailings, soils |
| Stratoni, GR | Active polymetallic sulphide mines (galena- <br> sphalerite-pyrite) with a mining history of <br> more than 2.500 years. | Waste rock |
| Montevecchio, <br> Monteponi, Sardinia, IT | Extensive Pb-Zn historic mining area. <br> Currently, there is one operating and many <br> redundant mines. | Sulphidic tailings, <br> calamina red mud, <br> soils |
| Estarreja, PT | Chemical industrial site. Production of <br> sulphuric acid by roasting of pyrites in the <br> 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 are being evaluated in field scale, include:

## a) Limestone or fly ash addition to prevent acid generation from sulphidic wastes

The technical objective is 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 the microscale, precipitation of reaction products around the pyrite grains, inhibiting further oxidation and/or on the 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 test work 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.

## b) Formation of surface barriers for the pyrite cinders and calamina residues

The technical objective is to develop an innovative, 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 is to achieve very low permeability of the surface layer in order to inhibit water infiltration and subsequent leaching of contaminants.

The laboratory work performed includes: 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 stabilising agents, and c) lysimeter kinetic tests.

## c) Chemical stabilisation of metals in oxidic wastes and soils

The technical objective is to develop a process for the in-situ immobilisation 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 stabilising 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. Stabilisation was examined by chemical extraction tests and verified by actual biological tests. Chemical extraction tests included toxicity characterisation using the EPA-TCLP test and determination of the bioavailable-phytotoxic fraction using a combination of EDTA, DTPA, and $\mathrm{NaHCO}_{3}$ leaching tests. The biological tests involved plant growth tests using dwarf beans (Phaseolus vulgaris starazagorski) as a 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.

### 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, $\mathrm{Na}_{2} \mathrm{H}_{2} \mathrm{EDTA}, \mathrm{Na}_{2} \mathrm{CaEDTA}$, and an acidic brine consisting of $\mathrm{HCl}-$ $\mathrm{CaCl}_{2}, \mathrm{~b}$ ) development of two integrated leaching processes based on the use of $\mathrm{Na}_{2} \mathrm{CaEDTA}$ and $\mathrm{HCl}-$ $\mathrm{CaCl}_{2}$ 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., and c) comparative evaluation of the above processes on representative soil samples from Montevecchio and Lavrion sites. The integrated $\mathrm{HCl}-\mathrm{CaCl}_{2}$ and $\mathrm{Na}_{2} \mathrm{CaEDTA}$ 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 SULPHIDIC 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 $18-20 \% \mathrm{w} / \mathrm{w}$ 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. 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. Field tests are currently in progress to assess the performance of above techniques under actual conditions.

### 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., $\mathrm{k}: \leq 10^{-7} \mathrm{~cm} / \mathrm{sec}$. Alternative materials, such as alumina red mud stabilised with gypsum and a sandbentonite mixture, are currently evaluated under field scale for the rehabilitation of calamina red muds and pyrite cinders respectively. Preliminary 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.

### 4.3 CHEMICAL STABILISATION OF METALS IN OXIDIC WASTES AND SOILS

For Lavrion oxidic tailings, phosphates, fly ash, and biological sludge, added to amounts $0.9,8$, and $10 \%$ $\mathrm{w} / \mathrm{w}$, 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 $7.5 \% \mathrm{w} / \mathrm{w}$ respectively. Alumina red mud stabilised with $5 \%$ gypsum was proven to be a successful stabilising agent for Montevecchio soils.

Given that inorganic materials (e.g., phosphates, fly ash, and 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.

### 4.4 LEACHING METHODS FOR THE CLEAN-UP OF CONTAMINATED SOILS

The $\mathrm{HCl}-\mathrm{CaCl}_{2}$ process was selected as the most efficient treatment option for Montevecchio soils, due to their low calcite content, whereas the $\mathrm{Na}_{2} \mathrm{CaEDTA}$ 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., $\mathrm{Pb} 93-95 \%$, $\mathrm{Zn} 78-85 \%$, $\mathrm{Cd} 71-95 \%$ 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 $1.6 \mathrm{~m}^{3}$ per ton soil.

## 5. COSTS

Cost estimates of rehabilitation technologies examined will be available upon evaluation of field-scale test results.

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| Project No. 5 |  |  |  |
| :---: | :---: | :---: | :---: |
| Application of Bioscreens and Bioreactive Zones |  |  |  |
| Location <br> Rademarkt (former dry cleaning site) <br> Rotterdam Harbour (oil refinery site) <br> 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 <br> In Situ <br> Bioremediation |
| Technical Contact <br> Huub Rijnaarts/Sjef Staps/ <br> Herco van Liere <br> TNO Institute of <br> Environmental Sciences, <br> Energy Research and Process <br> Innovation <br> Laan van Westenenk 501 <br> 7334 DT Apeldoorn <br> The Netherlands <br> Tel: +31555493380 <br> Fax: +31555493523 <br> E-mail: <br> H.H.M.Rijnaarts @ mep.tno.nl <br> S.Staps@mep.tno.nl <br> H.C.vanLiere@mep.tno.nl | Project Dates Accepted 1998 <br> Costs Documented? Yes | Media <br> Groundwater <br> Project Size <br> 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 costeffective 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. The source area contains high concentrations of PCE and needs to be treated to prevent subsequent delivery to the plume area. Source remediation and plume interception were therefore required. Analyses have shown insufficient natural biodegradation capacity due to a shortage of intrinsic electron donor. Therefore a 50 m semi full-scale reactive zone has been installed in the source zone. Results after 7 months have shown complete biodegradation of PCE to ethene and ethane.

Oil refinery site. At this site in the Rotterdam Harbour area, it is required to manage a plume (>200 m up to a depth of 4 m ) of the dissolved fraction of a mineral oil/gasoline contamination ( $80 \%$ of the compounds belong to the $\mathrm{C} 6-\mathrm{C} 12$ fraction). The redox conditions are anaerobic and the natural biodegradation capacity is unknown, but probably insignificant. To protect further spreading into the harbour 3 types of bioscreens, pilot-scale sparging applications, were installed. The dimensions of each pilot is 40 m by 0.4 m by 4 m deep. One bioscreen has been trenched and backfilled with gravel. The other two bioscreens are vertical and horizontal air sparging fences. Results after one year is a total biodegradation up to $70 \%$. From 2001 the airsparging will be intensified and monitored.

Aromatic hydrocarbon (BTEX) sites. At three sites (> 250 m length and $10-80 \mathrm{~m}$ depth) in the northern part of the Netherlands, deep anaerobic aquifers contaminated with Benzene, Toluene, Ethylbenzene or Xylenes (BTEX) have been investigated. Under the existing sulphate-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, probably due to absence of adapted micro-organisms. Managing the benzene plumes, i.e., by enhanced in-situ bioprocesses, is therefore required. Infiltration of electron acceptors was investigated, for example minimal amounts of oxygen combined with nitrate. Push-pull experiments at the site have shown complete biodegradation of BTEX. From 2001 pilot-scale application and monitoring is planned.

Chlorinated pesticides site. Hexachlorocyclohexane (HCH) isomers are important pollutants introduced by the production of lindane (gamma HCH ). The redox conditions are mixed: sulphate reducing to iron reducing. Natural degradation of all HCH -isomers was demonstrated at the site of investigation and in the laboratories of TNO. To minimise all risks interception of the HCH/Chlorobenzene/benzene plume ( $>250$ m length, up to a depth of 18 m ) was needed to protect the canal located at the boundary of the industrial site. The in situ bioremediation concept investigated at this site is integrated into new infrastructural plans of a large transhipment facility. The semi full-scale design was constructed in 2000 and contains of 2 sequential bioscreens upstream. Here electron donor will be infiltrated and extracted and biological biodegradation of HCH into monochlorobenzene and benzene will be monitored with monitoring filters. Downstream an above ground (bio)reactor system is set up. Here the groundwater is extracted and monochlorobenzene and benzene is mineralised. From 2001 testing of the complete system starts.

## 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. Microcoms 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-andtreat 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 complete evaluations of technology performance are to be expected at the end of 2001.

## 5. COSTS

In a separate cost-analyses project, the costs of investment and operation of various bioscreen configurations (i.e., the funnel-and-gate ${ }^{\mathrm{TM}}$, 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 ${ }^{\mathrm{TM}}$ 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 ${ }^{\mathrm{TM}}$ 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.

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| Project No. 6 |  |  |  |
| :---: | :---: | :---: | :---: |
| Rehabilitation of a Site Contaminated by PAH Using Bio-Slurry Technique |  |  |  |
| Location <br> Former railroad unloading area, northern Sweden | Project Status Interim | Media Soil | Technology Type Ex situ bioremediation |
| Technical Contact Erik Backlund Eko Tec AB Näsuddsvägen 10 93221 Skelleftehamn Sweden tel: +46/910-33366 fax: +46/910-33375 | Project Dates  <br> Accepted 1996 <br> Final Report 2001 <br> Costs Documented? | Contaminants coal tars, phenols, cyan ammonium compounds | es, metals, |
| E-mail: erik.backlund@ebox.tninet.se | No | Full-scale (3,000 tons) | Yes |

Please note that this project summary was not updated since the 1998 Annual Report.

## 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 creosotecontaminated 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 PROCESSS

### 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 $>2 \mathrm{~mm}$ were separated from the process. The remaining soil fraction ( $<2 \mathrm{~mm}$ ) was pumped to a $60 \mathrm{~m}^{3}$ slurryphase bioreactor for further treatment. The volume of the treated soil fraction ( $<10 \mathrm{~mm}$ ) was approximately $25 \mathrm{~m}^{3}$. Samples were taken from the soil before water was added.

### 3.2 Slurry-Phase Bioreactor Treatment

Slurry-phase treatment was carried out in a $60 \mathrm{~m}^{3}$ 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 ( $<2 \mathrm{~mm}$ 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.

| Risk Assessment for a Diesel-Fuel Contaminated Aquifer Based on Mass Flow Analysis During Site Remediation |  |  |  |
| :---: | :---: | :---: | :---: |
| Location Menziken / Studen, Switzerland | Project Status Final | Media <br> Groundwate | Technology Type In situ Bioremediation |
| Technical Contact <br> Mathias Schluep <br> Frohburgstrasse 184 | Project Dates <br> Accepted 1997 <br> Final Report 2000 | Contaminants <br> Petroleum Hydrocarbons (Diesel Fuel, Heating Oil) |  |
| 8057 Zurich <br> Switzerland <br> tel: +41-79-540-5557 <br> mathias@schluep.ch | Costs Documented? No | Project Size | $\begin{aligned} & \text { Results Available? } \\ & \text { Yes } \end{aligned}$ |
| Christoph Munz <br> BMG Engineering Ltd <br> Ifangstrasse 11 <br> 8057 Schlieren <br> Switzerland <br> tel: +41-1-732-9277 <br> fax: +41-1-730-6622 <br> E-mail: christoph.munz@bmgeng.ch <br> Josef Zeyer <br> Soil Biology <br> Inst. of Terrestrial Ecology ETHZ <br> Grabenstrasse 3 <br> 8952 Schlieren <br> Switzerland <br> tel: +41-1-633-6044 <br> fax: +41-1-633-1122 <br> E-Mail: zeyer@ito.umw.ethz.ch |  |  |  |

## 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 $(\mathrm{PAH})$, 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 (Figure 8): dissolution of PHCs into the aqueous phase (section A), anaerobic (section B) and aerobic biodegradation (section C) of the dissolved compounds.


Figure 8: 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

## 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.

## 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 (Figure 8, section A). 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.

## 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 (Figure 8, 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 9. 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 (Figure 8) 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 (Figure 8) using the corresponding concentrations of the relevant compounds as well as their toxicological properties. The non-cancerogenic risk (Figure 10) as well as the cancerogenic 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 10: 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.

Figure 9: 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.

## 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:

1. 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).
2. 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.
3. 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.
4. 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.

## 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.

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| 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 <br> Istanbul University | Project Status Interim Report | Contaminants <br> Heavy metals ( $\mathrm{Pb}, \mathrm{Cu}$, Cd ) and radionuclides $\left({ }^{137} \mathrm{Cs},{ }^{90} \mathrm{Sr},{ }^{238} \mathrm{U}\right)$, textile dyes | Technology Type In situ adsorption and stabilization/ solidification |
| Technical Contact Resat Apak Istanbul University Avcilar Campus, Avcilar 34850 Istanbul, Turkey | Project Dates <br> Accepted 1998 <br> Interim Report 1999 <br> Final Report 2001 | Media <br> Soil and groundwater (Unconventional sorbents e.g., red muds and fly ashes, simulate hydrous oxide-like soil minerals; kaolinite and feldspar represent clay minerals) |  |
| Tel: 90/212-591-1996 <br> Fax: 90/212-591-1997 <br> E-mail: <br> rapak@istanbul.edu.tr | Costs Documented? <br> No | Project Size Bench-scale | Results Available? <br> Partly |

Please note that this project summary was not updated since the 1999 report. An update will be provided in the 2001 report.

## 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 cementbased 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 ( $\mathrm{Pb}, \mathrm{Cd}, \mathrm{Cu}, \mathrm{Cr}, \mathrm{U}$, 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, ${ }^{137}$ Cs 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 ${ }^{90} \mathrm{Sr}$ contamination. Land burial of low-level radioactive wastes also pose 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 $\mathrm{Pb}(\mathrm{II}), \mathrm{Cd}(\mathrm{II})$ and $\mathrm{Cu}(\mathrm{II})$, 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 (coalfired) 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/ $\mathrm{N}_{2}$ surface area analysis, and their surface acidity constants $\left(\mathrm{pK}_{\mathrm{a}}\right)$ 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 $\mathrm{Cs}-137$ and $\mathrm{Sr}-90$ 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 ( $4 \times 4 \times 16 \mathrm{~cm}^{3}$ ), 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 $50-200 \mathrm{mg} \mathrm{Cd}. \mathrm{~g}^{-1}, 40-100 \mathrm{mg} \mathrm{Cu} . \mathrm{g}^{-1}$, and $100-350 \mathrm{mg} \mathrm{Pb} . \mathrm{g}^{-1}$.

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 were as follows in terms of molar saturation capacities: $\mathrm{Cu}>\mathrm{Pb}>\mathrm{Cd}$ for fly ashes and $\mathrm{Cu}>\mathrm{Cd}>\mathrm{Pb}$ for red muds. The degree of insolubility of the metal hydroxides approximately followed the same order. The simulation of $\mathrm{CO}_{2}$-injected groundwater conditions were achieved by saturated aqueous $\mathrm{CO}_{2}(\mathrm{pH} 4.8)$ and carbonic acid/bicarbonate buffer ( pH 7.0 ) solutions. The heavy metals $(\mathrm{Cu}, \mathrm{Pb}, \mathrm{Cd})$ 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 solidifed concrete blocks over extended periods, with the exception of $\mathrm{Cu}(\mathrm{II})$, which reached a concentration of 0.4 ppm after 8 months in a water leachate of $\mathrm{pH} 8-9.2 \%$ setting accelerator $\mathrm{Ca}_{3}\left(\mathrm{PO}_{4}\right)_{2}$-added improved formulations could bear only $10 \%$ of lead-loaded fly ash, while this tolerance could be raised to $20 \%$ fly ash by incorporating ( $3 \% \mathrm{Ca}_{3}\left(\mathrm{PO}_{4}\right)_{2}+1 \% \mathrm{CaCl}_{2}$ ) 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 $10-100 \mathrm{ppm}$ 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 $\mathrm{Fe}_{2} \mathrm{O}_{3}, \mathrm{Al}_{2} \mathrm{O}_{3}, \mathrm{SiO}_{2}, \mathrm{TiO}_{2}$ 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., $\mathrm{Cd}^{2+}, \mathrm{Pb}^{2+}$ (and partly $\mathrm{Cu}^{2+}$ ) and $\mathrm{Cd}-\mathrm{EDTA}^{2-}, \mathrm{Pb}^{2} \mathrm{EDTA}^{2-}$, $\mathrm{Cu}-\mathrm{EDTA}^{2-}$, 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 $\mathrm{m}^{2}$ for 1 m 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 ( $\mathrm{Pb}, \mathrm{Cu}, \mathrm{Cd}$ ) and radionuclide ( $\mathrm{Cs}-137$ and $\mathrm{Sr}-90$ ) 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.

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| Project No. 9 |  |  |  |
| :---: | :---: | :---: | :---: |
| Solidification/Stabilization of Hazardous Wastes |  |  |  |
| Location <br> Middle East Technical University, Ankara, Turkey | Project Status <br> Near completion | Media <br> Soil, mining waste, and wastewater and sludge from pulp and paper industry | Technology Type Solidification/ stabilization |
| Technical Contact <br> Kahraman Ünlü <br> Middle East Technical <br> University <br> Environmental Engineering <br> Department <br> 06531 Ankara <br> Turkey | Project Dates <br> Accepted 1998 <br> Final Report 2001 | Contaminants PCBs, AOX (adsorbable organic halides), heavy metals |  |
| Fax: 90-312-210-1260 <br> E-mail: kunlu@metu.edu.tr | Costs Documented? No | Project Size Bench-scale | Results Available? Partially |

## 1. INTRODUCTION

Solidification and stabilization are treatment processes designed to either improve waste handling and physical characteristics, decrease the surface area across which pollutants can transfer or leach, or limit the solubility or 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 $\mathrm{S} / \mathrm{S}$ 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 regulation of the Control of Hazardous Wastes (C of HW) 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 existing hazardous wastes and their safe disposal in compliance with the current regulation. The Solidification/Stabilization (S/S) technology is recognized by the Turkish regulation of the C of HW 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, and measuring microstructural characteristics of, 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 residue material from gold mining has relatively high heavy metal content, in order to observe the performance of S/S technology effectively, much more concentrated waste in terms of heavy metal concentration was considered to be useful. Concentrated mine waste was obtained by the addition of the salts of some heavy metals.

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. Mixing ratios for different waste groups are given in Table1.

Table 1: Waste material and portland cement mixing ratios.

| Waste Material | Cement Percentage |
| :--- | :--- |
| Residue material from gold mining (fine and coarse) | 10 and 20\% |
| PCBs contaminated soil | 20 and 35\% |
| Wastewater (ww) from pulp and paper industry | $1: 6$ and 1:8 (ww:cement) |
| Sludge from treatment of pulp and paper industry <br> wastewater | 30 and 50\% |

## 4. ANALYTICAL APPROACH

Before solidification, physical and rheological characteristics of all wastes, except wastewater, were determined through Atterberg limits, maximum dry density, optimum moisture content, specific gravity, and particle size distribution determinations. After these measurements, the samples were prepared for the 28 day-cure for solidification by compacting the desired waste:cement mixture-at its optimum moisture content corresponding to its maximum dry density-in cylindrical molds having a height of 71 mm and a diameter of 36 mm .

Physical tests and measurements were performed on these solidified samples. The unconfined compressive strength tests were performed using triaxial shear apparatus and saturated hydraulic conductivities of solidified duplicate samples were measured using a flexible wall permeameter. At the end of the cure period-prior to the performance of leaching tests-samples were crushed and then passed through sieves for fractionation to sizes greater than 2 mm and between $1-2 \mathrm{~mm}$. The U.S. EPA's

Toxicity Characteristic Leaching Procedure (TCLP) and distilled water leaching procedure were applied using 2 and 3 grams of waste sample from each size fraction. On the leachate obtained by two different leaching procedures, pH and concentrations of the following contaminants were measured: $\mathrm{Cd}, \mathrm{Cr}, \mathrm{Cu}$, $\mathrm{Fe}, \mathrm{Pb}, \mathrm{Zn}, \mathrm{Al}, \mathrm{Ca}, \mathrm{Mg}, \mathrm{Na}, \mathrm{K}, \mathrm{Cl}, \mathrm{SO}_{4}, \mathrm{CO}_{3}$ and $\mathrm{PO}_{4}$. Heavy metals were analyzed by flame atomic absorption spectrophotometer, chloride and carbonate ions by titrimetric methods and sulfate and phosphate by spectrophotometric methods. Based on the results of the physical tests and the leachate compositions obtained from solidified samples, for each waste type, the effectiveness of the S/S technology in terms of contaminant encapsulation was assessed. For all chemical analyses, U.S. EPA SW-846 standard methods were used.

## 5. RESULTS

Initial total metal analyses of gold mining residue material showed that heavy metal $(\mathrm{Cd}, \mathrm{Cr}, \mathrm{Cu}, \mathrm{Pb}$, and Zn ) concentrations were relatively high except for cadmium. However, in order to observe the performance of S/S technology effectively, much higher heavy metal concentrations were required. Therefore, nitrate or sulfate salts of these heavy metals were added to the gold mining residue. By the additions of metal salts, original metal concentrations in the waste were increased approximately 1000 $\mathrm{mg} / \mathrm{kg}$ for each metal. Because cement, as a binding agent, was mixed with waste material, metal composition of cement was also determined to see any contribution to metal content of waste. The results of total metal analyses for cement are given in Table 2. As seen from the table, $\mathrm{Cd}, \mathrm{Cr}, \mathrm{Cu}$, and Pb are not present in cement.

Table 2: Initial metal composition of mining waste and portland cement

| Metals | Waste $(\mathbf{m g} / \mathbf{g})$ | Cement $(\mathbf{m g} / \mathbf{g})$ |
| :--- | :--- | :--- |
| Cd | 0.04 | 0 |
| Cu | 2.41 | 0.03 |
| Cr | 0.35 | 0.50 |
| Pb | 3.48 | 0 |
| Zn | 2.38 | 0.04 |
| Fe | 29.70 | 15.63 |
| Al | 37.89 | 29.07 |
| Ca | 0.44 | 276.31 |
| Mg | 1.15 | 8.24 |

Before the 28 day-cure period, additional tests also were performed to determine some physical and the rheological characteristics of the waste:cement mixture. By these tests, Atterberg limits, maximum dry density, optimum moisture content, specific gravity, particle size distribution of each case were determined. Results are given in Table 3.

Table 3: Physical and rheological characteristics of fine and coarse gold mining waste and cement mixtures

| Characteristics | $\mathbf{1 0 \%}$ cement <br> (fine) | $\mathbf{2 0 \%}$ cement <br> (fine) | $\mathbf{1 0 \%}$ cement, <br> (coarse) | $\mathbf{2 0 \%}$ cement, <br> (coarse) |
| :--- | :---: | :---: | :---: | :---: |
| Dry density (g/ml) | 1.77 | 1.78 | 2 | 2 |
| Opt. Moisture (\%) | 15 | 17 | 10 | 11 |
| Liquid limit (\%) | 27.8 | 27.9 | 21.75 | 22.1 |
| Plastic limit (\%) | 18.05 | 20.55 | 17.05 | 16.05 |
| Plasticity index (\%) | 9.75 | 7.35 | 4.7 | 6.05 |
| Soil classification | ML (silt-low <br> plasticity) | ML(silt-low <br> plasticity) | SM (silty sands) | SM(silty sands) |
| Specific gravity | 2.72 | 2.73 | 2.67 | 2.745 |
| Particle size | $18 \%$ clay | $22 \%$ clay | $12 \%$ clay | $13 \%$ clay |
| Distribution | $55 \%$ silt | $52 \%$ silt | $29 \%$ silt | $29 \%$ silt |
|  | $27 \%$ sand | $26 \%$ sand | $59 \%$ sand | $58 \%$ sand |

The metal composition of the waste samples also was determined by the acid digestion method. Results are given in Table 4.

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

| Metals \& Ions | $\mathbf{1 0 \%}$ cement, fine | $\mathbf{1 0 \%}$ cement, coarse | $\mathbf{2 0 \%}$ cement, fine | 20\% cement, coarse |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Cd}(\mathrm{mg} / \mathrm{g})$ | 1.25 | 0.85 | 1.00 | 0.75 |
| $\mathrm{Cu}(\mathrm{mg} / \mathrm{g})$ | 3.33 | 1.69 | 2.55 | 1.25 |
| $\mathrm{Cr}(\mathrm{mg} / \mathrm{g})$ | 3.06 | 1.92 | 2.14 | 1.77 |
| $\mathrm{~Pb}(\mathrm{mg} / \mathrm{g})$ | 3.09 | 1.42 | 2.32 | 1.21 |
| $\mathrm{Zn}(\mathrm{mg} / \mathrm{g})$ | 1.90 | 1.35 | 1.99 | 1.05 |
| $\mathrm{Fe}(\mathrm{mg} / \mathrm{g})$ | 13.50 | 10.47 | 13.31 | 8.78 |
| $\mathrm{Al}(\mathrm{mg} / \mathrm{g})$ | 26.13 | 11.17 | 24.36 | 8.25 |
| $\mathrm{Ca}(\mathrm{mg} / \mathrm{g})$ | 7.83 | 15.54 | 17.72 | 19.4 |
| $\mathrm{Mg}(\mathrm{mg} / \mathrm{g})$ | 1.71 | 3.1 | 2.49 | 1.56 |
| $\mathrm{~K}(\mathrm{mg} / \mathrm{g})$ | 21.55 | 9.95 | 12.95 | 9 |
| $\mathrm{Na}(\mathrm{mg} / \mathrm{g})$ | 7.78 | 5.15 | 2.0 | 8.9 |
| $\mathrm{SO}_{4}^{-2}(\mathrm{mg} / \mathrm{l})$ | 575.3 | 257.5 | 520.3 | 158.3 |
| $\mathrm{PO}_{4}^{-3}(\mathrm{mg} / \mathrm{l})$ | 5.93 | 10.87 | 20.1 | 12.15 |
| $\mathrm{Cl}^{-}(\mathrm{mg} / \mathrm{l})$ | 494.95 | 849.7 | 1174.6 | 699.8 |
| $\mathrm{CO}_{3}^{-2}(\mathrm{mg} / \mathrm{l})$ | 5232 | 5475 | 7320 | 9660 |

Note that metal concentrations of coarse waste samples were diluted due to the addition of sand, which shifted the texture of waste from silt (fine) to sand (coarse). Due to high concentrations of $\mathrm{Fe}, \mathrm{Al}$, Ca , and Mg in the portland cement, waste samples also have very high concentrations of these metals.

At the end of the cure period, TCLP and distilled water leaching procedure were applied and leachate obtained for each waste group was analyzed for heavy metals and some ions. Results of these analyses are given in Table 5.

Table 5: The chemical compositions of leachates obtained from mining waste using TCLP and distilled water leaching procedures

| $\begin{aligned} & \text { Ions } \\ & (\mathrm{mg} / \mathrm{l}) \end{aligned}$ | 10\% cement, fine |  |  |  | 20\% cement, fine |  |  |  | 10\% cement, coarse |  |  |  | 20\% cement, coarse |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\mathbf{1 - 2 ~ m m ~}$ |  | >2 mm |  | $\mathbf{1 - 2 ~ m m ~}$ |  | >2 mm |  | $\mathbf{1 - 2 ~ m m ~}$ |  | >2 mm |  | $\mathbf{1 - 2 ~ m m ~}$ |  | >2 mm |  |
|  | TCLP | Water | TCLP | Water | TCLP | Water | TCLP | Water | TCLP | Water | TCLP | Water | TCLP | Water | TCLP | Water |
| 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 |
| $\mathrm{SO}_{4}{ }^{2-}$ | 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 |
| $\mathrm{PO}_{4}{ }^{3-}$ | 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 |
| $\mathrm{Cl}^{-}$ | 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 |
| $\mathrm{CO}_{3}{ }^{2-}$ | 1854 | 4320 | 1320 | 1440 | 1110 | 2370 | 300 | 4020 | 2940 | 1350 | 1500 | 630 | 495 | 780 | 735 | 150 |

ND: Concentration is below the detection limit (for $\mathrm{Cd}, 0.05 \mathrm{mg} / \mathrm{l} ; \mathrm{Cu}, 0.05 \mathrm{mg} / \mathrm{l} ; \mathrm{Cr} 0.1 \mathrm{mg} / \mathrm{l} ; \mathrm{Pb} 0.1 \mathrm{mg} / \mathrm{l} ; \mathrm{Fe}, 0.5 \mathrm{mg} / \mathrm{l} \mathrm{and} \mathrm{Al}, 5 \mathrm{mg} / \mathrm{l}$ )
In general, the following observations can be made from Table 5. Metal concentrations in TCLP leachate are significantly higher than the metal concentrations in distilled water leachate. At the same cement ratio, fine waste samples produce leachate having lower metal concentrations than coarse waste samples. Increasing cement ratio does not have any considerable effect on metal concentrations in the leachate. Comparisons with EPA toxicity characteristic limits, which are given as $1 \mathrm{mg} / \mathrm{l}$ for $\mathrm{Cd}, 5 \mathrm{mg} / \mathrm{l}$ for Cr and Zn , and $130 \mathrm{mg} / \mathrm{l}$ for Cu , indicate that only Cd concentrations in the leachate from waste samples of $10 \%$ cement ratio exceed the regulated level. All the other metal concentrations in the leachate do not exceed the regulated levels. With regard to crashing effect on metal concentrations in the leachate, results show that solidified samples crashed to form particle sizes $>2 \mathrm{~mm}$ produce lower metal concentrations in distilled water leachate compared to solidified samples crashed to form particle sizes between 1-2 mm . In the case of TCLP leachate, the same situation was observed only for coarse waste sample with $20 \%$ cement ratio. For other samples, crashing the solidified samples into different particle sizes did not affect the metal concentrations in the TCLP leachate.

Besides leaching tests, unconfined compressive strength and hydraulic conductivity tests were performed on duplicate cylindrical solidified samples of each treatment. The results of unconfined compressive strength and hydraulic conductivity measurements are given in Table 6.

Table 6: Unconfined compressive strength and hydraulic conductivity results for mine waste samples with different cement ratios

| Property | $\mathbf{1 0 \%}$ cement <br> (fine) | $\mathbf{2 0 \%}$ cement <br> (fine) | $\mathbf{1 0 \%}$ cement <br> (coarse) | $\mathbf{2 0 \%}$ cement <br> (coarse) |
| :--- | :---: | :---: | :---: | :---: |
| Uncon. Comp. Strength, kPa | 1153.46 | 2520.4 | 1019 | 3250 |
| Hydraulic Conductivity, $\mathrm{m} / \mathrm{s}$ | $2.1 * 10^{-9}$ | $1.09 * 10^{-9}$ | $1.84 * 10^{-9}$ | $1.04 * 10^{-9}$ |

Results show that as cement ratio and the coarse fraction in the waste increase, unconfined compressive strength also increase. At the same cement ratio, solidified fine and coarse waste materials have similar hydraulic conductivity values. However, as the cement ratio increases, hydraulic conductivity values decrease significantly both for fine and coarse samples.

At this point, both physical and chemical analyses concerning the solidification/stabilization of metals in the mining waste were completed. The other aspects of the project (the study on PCB-contaminated soil and adsorbable organic halides, and AOX-containing wastewater and sludge) are currently under way. Completed parts are explained below.

Concentration of AOX in wastewater and sludge obtained from the pulp and paper industry were measured. AOX concentrations were $39 \mathrm{mg} / \mathrm{l}$ in wastewater and $0.4 \mathrm{mg} / \mathrm{g}$ in sludge. Wastewater was mixed with cement at two different ratios (1:6 and 1:8), which bound the optimum moisture content of cement yielding maximum dry density. Samples were prepared for the 28 day-S/S cure by compacting the wastewater:cement mixtures in cylindrical molds having a height of 71 mm and a diameter of 36 mm . At the end of cure period, unconfined compressive strength measurements were done on duplicate solidified samples. The results are 5800 kPa and 5350 kPa for 1:6 and 1:8 wastewater:cement ratios, respectively, which indicate that 1:6 wastewater to cement ratio yields stronger solid blocs. After the strength measurements were taken, the TCLP was applied using solidified samples that were crushed to form particle sizes $>2 \mathrm{~mm}$ and between $1-2 \mathrm{~mm}$. The results of AOX measurements in TCLP leachate are given in Table 7. Results show that the cement-mixing ratio and the crushing of the solidified samples into different particle sizes did not affect the AOX concentration in the TCLP leachate. After solidification with portland cement, nearly $90 \%$ reduction in AOX concentration of wastewater is achieved. Similar leaching tests have currently been conducted using distilled water as well.

Table 7: AOX concentrations in TCLP leachate obtained from solidified wastewater samples of two different cement ratios and crashed particle sizes

| Treatment | AOX Concentration (mg/L) |  |
| :--- | :---: | :---: |
|  | $\mathbf{1 - 2 ~ m m}$ | $\mathbf{> 2 m m}$ |
| 1:6 ww:cement | 3.24 | 3.33 |
| 1:8 ww:cement | 3.20 | 3.35 |

Analysis involving PCB contaminated soil and pulp and paper sludge are currently underway. Sludge samples were mixed with portland cement at the ratios of $30 \%$ and $50 \%$. Both soil and sludge samples are currently going through a 28 day-S/S curing period.

## 6. HEALTH AND SAFETY

Not applicable.

## 7. ENVIRONMENTAL IMPACTS

Not applicable.

## 8. COSTS

Not available.

## 9. CONCLUSIONS

When the results of leaching procedures are compared with the limiting values specified by the Turkish regulation of the Control of Hazardous Wastes (C of HW), metal concentrations in the leachate are within the acceptable range. Therefore, wastes with metal concentration levels similar to the mining waste considered in this study can be disposed of in landfills. According to the U.S. EPA regulations, the concentrations of heavy metals in TCLP leachate are below the specified toxicity limits, except for cadmium. When the crushed size of solidified samples is taken into consideration, in general the crushed samples with finer size $(1-2 \mathrm{~mm})$ yield higher metal concentrations in the leachate. This is probably due to the increase in the surface area of crushed samples that contact the leachant.

As performance criteria, besides leachate concentrations, the results of physical tests are also important. According to the U.S. EPA standards, minimum value of unconfined compressive strength is 350 kPa for the disposal of solidified hazardous wastes in landfills. Unconfined compressive strength values measured for all treatments considered in this study are well above this limiting value. Therefore, these solidified samples easily can be disposed of in landfills. Hydraulic conductivity values measured for all treatments are in the order of $10^{-9} \mathrm{~m} / \mathrm{s}$, although higher cement addition ( $20 \%$ ) results in lower conductivity values. Measured conductivity values are four orders of magnitude lower than the value of $10^{-5} \mathrm{~cm} / \mathrm{s}$ recommended by U.S. EPA for land-burial of stabilized wastes (EPA, 1986).

Technical criteria for the performance assessment of S/S require low leachate concentrations, low permeability, and high unconfined compressive strength. For metal-containing mine 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 was mixed with the waste consisting of nearly $75 \%$ fine (silt and clay size) particles.

The application of S/S for AOX in wastewater also gave successful results, with the achievement of nearly $90 \%$ reduction in AOX concentration in the leachate.

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| Project No. 10 |  |  |  |
| :---: | :---: | :---: | :---: |
| Metal-Biofilm Interactions in Sulphate-Reducing Bacterial Systems |  |  |  |
| Location Under development in consortium's laboratories | Project Status Final Report | Contaminants Metals | Technology Type Biological <br> Treatment |
| Technical Contact <br> Prof. Harry Eccles <br> BNFL, <br> Research \& Technology, Springfields, Preston, Lancashire PR4 0XJ, UK | Project Dates <br> Project accepted $1998$ <br> Final project report $1999$ | Media Effluents/Ground water |  |
| Tell 441772762566 <br> Fax 441772762891 <br> E-mail he1@bnfl.com | Costs Documented? <br> No | Project Size Laboratory | Results Available? Yes |

Project 10 was completed in 1999.

## 1. INTRODUCTION

The development of Sulphate-Reducing Bacteria 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:

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


## 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 favoured 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 characterisation 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.

## 1. 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:

The separation of carbon source, or sulphate or heavy metal from the SRB biofilm.
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.
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.

## 2. 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 $20-100 \mu \mathrm{~m}$. This appeared to primarily affect the area available for attachment.

Temperature (maximum growth at $30^{\circ} \mathrm{C}$ ), and the substrate concentration also affected growth and sulphate reduction significantly and $\mathrm{K}_{\mathrm{m}}$ 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 $500 \mu \mathrm{~m}$ with deeper material appearing to be inactive.

### 2.1 Substrate Utilisation

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-utilisation 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 utilised, producing acetate. Varying the concentrations over a 10 - to 20 -fold range and allowed determination of lactate utilisation kinetics, which was carried out by personnel engaged on process modeling ( $\mathrm{K}_{\mathrm{m}} @ 1,4 \mathrm{mM}$ ). Acetate was utilised very slowly by the biofilm culture and accumulated during experiments on lactate utilisation as it was produced by SRB metabolising lactate.

When acetate was supplied as the sole carbon/energy source, its rate of utilisation and the accompanying sulphate reduction were almost undetectable so that no kinetic parameters could be determined. The low acetate utilisation 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-utilising mixed SRB culture was obtained, combined with the lactate-utilising culture and the combined culture was maintained on mixed lactate and acetate as carbon/energy source. This combined culture utilised 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-utilising culture led to increased acetate utilisation, it appears that the very low rate of acetate utilisation in the original culture was due to the absence of acetate-degrading organisms.
2.2 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 $500 \mu \mathrm{~m}$ ) 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.

## 3. Metal Precipitation studies

### 3.1 Metal $(\mathrm{Cd}$ 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 parameterise 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 $(250 \mu \mathrm{M})$, almost all metal was precipitated with a small colloidal phase and almost no remaining dissolved metal At 500 and $1000 \mu \mathrm{M}$ 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.

### 3.2 Iron precipitation

The degree of iron sulphide formation by the biofilm (not previously exposed to FeSO ) was found to depend upon the initial FeSO4 loading of the medium, with a saturating concentration 0.5 mM FeSO 4 . Under these conditions $0.86 \mathrm{mg} / \mathrm{cm}^{2}$ 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 $\mathrm{S}^{-}$in solution.

## 4. Membrane Studies

### 4.1 Permeable membrane

Investigations into the flow characterisation of the 2.5 mm 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 ( $>0.05 \mathrm{mil} / \mathrm{min} / \mathrm{cm} 2$ ) 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.
4.2 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 bulkphase 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 metalcontaining 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.

5 Modelling Studies

### 5.1 Biofilm

A model of the biological phenomena occurring within the sulphate reducing bacterial biofilms, has been developed. The model is based upon the Generalised 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 modelling 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 utilised as input data by the chemical speciation component of the code, PHREEQE.

The main roles of PHREEQE are the modelling 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 utilisation 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 utilised 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 modelling tasks in the future, taking advantage of the full extent of it capabilities.

### 5.2 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:

- Sulphide production is zero order in sulphate concentration and exhibits a Monod rate dependence on carbon substrate composition (ignoring complications from acetate utilisation),
- 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,
- 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,
- 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 realised at the outset of the project and has not, hitherto, been discussed or analysed in the literature. Nonetheless, the experimental and theoretical work in the project has:

- 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),
- Allowed estimates of the rate of biofilm capture of colloidal material to be made, and
- 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 <br> Operational coal tar processing and organic chemicals manufacturing plant, West Midlands, U.K. | Project Status Final report | Media <br> Groundwater | Technology Type <br> Intrinsic <br> bioremediation, natural attenuation |
| Technical Contact <br> Dr. Steve Thornton, <br> Groundwater Protection \& Restoration Group, <br> Dept. of Civil \& Structural Engineering, University of Sheffield, Mappin St., <br> SHEFFIELD S1 3JD <br> United Kingdom | Project Dates  <br> Accepted 1998 <br> Final Report 1999 | Contaminants Coal tars, phen BTEX | , cresols, xylenols, |
| Tel: 01142225744 <br> Fax: 01142225700 <br> E-mail: s.f.thornton@sheffield.ac.uk | 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 $\mathrm{NH}_{4}$ ), 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 $12,500 \mathrm{mg} \mathrm{l}^{-1}$. The aquifer is naturally aerobic, calcareous at depth and contains abundant Fe and Mn oxides as grain coatings. Groundwater levels are shallow (typically <5mbgl) and the aquifer is 250 m thick in the vicinity
of the site. Groundwater flow is $4-11 \mathrm{~m} \mathrm{y}^{-1}$. The current volume of the plume is about 3 million $\mathrm{m}^{3}$. The total concentration of organic compounds in the plume source area is presently $24,800 \mathrm{mg} \mathrm{l}^{-1}$, including $12,500 \mathrm{mg}^{-1}$ 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 $\mathrm{SO}_{4}$ plume with concentrations up to $449 \mathrm{mg} \mathrm{l}^{-1}$. 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 modelling 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 modelling of biodegradation processes in the plume is ongoing. An initial modelling study was undertaken with the biodegradation code, BIOREDOX, to test the conceptual process model of the plume and to identify additional modelling objectives. Further transport modelling 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 modelling 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 fieldscale.

## 4. ANALYTICAL APPROACH

Groundwater samples have been collected, anaerobically, for analysis of organic contaminants, dissolved gases (e.g., $\mathrm{N}_{2}, \mathrm{CO}_{2}, \mathrm{CH}_{4}$ ), major cations, major anions, organic and inorganic (e.g., total inorganic carbon, $\mathrm{Fe}^{2+}, \mathrm{Mn}^{2+}, \mathrm{S}^{2-}$ ) metabolites of phenolic compound degradation, nutrients, ${ }^{34} \mathrm{~S}{ }^{\beta 2} \mathrm{~S}-\mathrm{SO}_{4},{ }^{34} \mathrm{~S} \mathrm{~S}^{\beta 2} \mathrm{~S}-\mathrm{S}^{2-}$, ${ }^{13} \mathrm{C} /{ }^{12} \mathrm{C}-\mathrm{CO}_{3}{ }^{2-},{ }^{18} \mathrm{O} /{ }^{16} \mathrm{O}-\mathrm{SO}_{4}$, 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 modelling 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 $\mathrm{NO}_{3}$ 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 ${ }^{34} \mathrm{~S} /{ }^{32} \mathrm{~S}-\mathrm{S}^{2-}$ and ${ }^{13} \mathrm{C} /{ }^{12} \mathrm{C}-\mathrm{CO}_{3}{ }^{2}$ - 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 $24,000 \mathrm{mg} \mathrm{L}^{-1}$. 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, fieldbased, technology which provide 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.

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| Project No. 12 |  |  |  |
| :---: | :---: | :---: | :---: |
| Treatability Test for Enhanced In Situ Anaerobic Dechlorination |  |  |  |
| Location | Project Status | Media | Technology Type |
| Cape Canaveral Air Station, FL | Interim Report | Groundwater | In Situ Bioremediation |
| Naval Air Station Alameda, CA |  |  |  |
| Fort Lewis, WA |  |  |  |
| To be determined |  |  |  |
| To be determined |  |  |  |
| Technical Contact | Project Dates | Contaminants |  |
| Lt. Lisa Ackert | Accepted 1999 | tetrachloroeth | ne (PCE) and |
| AFRL/MLQ | Final Report 2001 | trichloroethyle | (TCE) |
| 139 Barnes Drive, Suite 2 |  |  |  |
| Tyndall AFB, FL 32403 |  |  |  |
| Tel: 850-283-6308 |  |  |  |
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| E-mail: lisa.ackert@mlq.afrl.af.mil |  |  |  |
| Catherine Vogel |  |  |  |
| DoD SERDP/ESTCP |  |  |  |
| Cleanup Program Manager |  |  |  |
| 901 N. Stuart Street, Suite 303 | Costs Documented? | Project Size | Results Available? |
| Arlington, VA 22203 | Soon | Field | Soon |
| Tel: (703) 696-2118 |  | Treatability |  |
| Fax: (703) 696-2114 |  | Testing |  |
| E-mail: vogelc@acq.osd.mil |  |  |  |

Please note that this project summary was not updated since the 1999 Annual Report.

## 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 $\left(\mathrm{H}_{2}\right)$ 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 $\mathrm{H}_{2}$ as an electron donor, and some can only use $\mathrm{H}_{2}$. Because more complex electron donors are broken down into metabolites and residual pools of $\mathrm{H}_{2}$ 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 $\mathrm{H}_{2}$ 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 $\mathrm{H}_{2}$ 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 determined.

## 3. TECHNICAL CONCEPT

## Site \#1: Cape Canaveral Air Station, FL

Site Description: Facility 1381, the Ordnance Support Facility at Cape Canaveral Air Station, contains a shallow, 110-acre volatile organic contaminant (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; however these contaminants have been detected in a surface water body adjacent to the site. This has prompted the state and federal environmental regulators to require a corrective measures study of various remedial options.

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 ft to 50 ft bgs, sands show a decrease in grain size and the silt and clay content increases. From 48.5 ft 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 $88.7 \mathrm{ft} / \mathrm{day}$. The pH of the groundwater ranged from 6.87 to 8.14 and conductivity readings ranged from 464 to 5,550 umhos $/ \mathrm{cm}$. The groundwater flow velocity has been calculated to be $0.21 \mathrm{ft} / \mathrm{day}$. The suspected source area contains high levels of TCE (up to $342 \mathrm{mg} / \mathrm{L}$ ) but TCE concentrations drop off quickly and only DCE and VC are detected towards the edges of the plume.

RABITT Testing: The ability of yeast extract, propionate, lactate, butyrate, and lactate/benzoate to stimulate anaerobic dechlorination of TCE was evaluated in laboratory microcosm studies using contaminated aquifer material. Butyrate and the lactate/benzoate mixture stimulated the complete conversion of TCE to ethene. Based on these laboratory results, the decision was made to proceed with the field treatability test.

The standard RABITT field treatability test design consists of an extraction/amendment/reinjection system within a small test plot. Contaminated groundwater is extracted near the end of the treatment plot, amended with nutrients and/or electron donor, and then reinjected near the head of the treatment plot. This design creates a hydraulic gradient to direct the flow of groundwater through the treatment plot. Multi-level monitoring points are placed within the treatment plot, in between the injection and extraction wells. Groundwater extraction and injection are optimized to achieve a 30 -day hydraulic residence time within the treatment plot.

This standard RABITT design had to be 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 above ground.

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. 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. The tri-level groundwater monitoring probes are positioned around the treatment cell to provide three-
dimensional data that are 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 modified system was installed at Facility 1381 in March 1999 and will operate for six months. The electron donor selected for field-testing was lactic acid. Lactic acid is added to the treatment cell at a concentration and flow rate to achieve an in situ concentration of 2-6 mM.

## Site \#2: Naval Air Station Alameda, CA

Site Description: Building 360 (Site \#4) at Naval Air Station Alameda was selected for the $2^{\text {nd }}$ 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 $30-70 \%$ solutions of sodium hydroxide. Site characterization activities performed by the facility revealed elevated levels of chlorinated solvents, primarily TCE ( 24 ppm ), DCE ( 8.6 ppm ) and VC ( 2.2 ppm ) detected between 5.5 and 15.5 feet bgs.

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

RABITT Testing: The ability of yeast extract, propionate, lactate, butyrate, and lactate/benzoate to stimulate anaerobic dechlorination of TCE was evaluated in laboratory microcosm studies using contaminated aquifer material. Yeast extract, butyrate, and lactate stimulated the complete conversion of TCE to ethene. Based on these laboratory results, the decision was made to proceed with the field treatability test.

The standard RABITT field treatability test was installed at the Alameda site. The system was installed in May 1999 and will operate for six months. The electron donor selected for field-testing was a mixture of butyric acid and yeast extract. Butyric acid and yeast extract are added to the treatment cell at a concentration and flow rate to achieve in situ concentrations of 3 mM butyric acid and $20 \mathrm{mg} / \mathrm{L}$ yeast extract.

## 4. 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.

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, $\mathrm{pH}, \mathrm{Fe}^{+2}$, conductivity, chloroethenes, dissolved organic carbon, ammonia, $\mathrm{CH}_{4}, \mathrm{C}_{2} \mathrm{H}_{4}, \mathrm{C}_{2} \mathrm{H}_{6}, \mathrm{NO}_{3}, \mathrm{NO}_{2}$, $\mathrm{SO}_{4}, \mathrm{Cl}, \mathrm{Br}$, alkalinity, and total iron.

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 <br> Site | Measurement Frequency |
| :--- | :--- | :--- |
| TCE, cis-DCE, VC, ethene | Lab | Initial, baseline, and biweekly |
| Volatile Fatty Acids (electron <br> 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 |
| $\mathrm{Fe}^{+2}$ | Field | Initial, baseline, and biweekly |
| $\mathrm{CH}_{4}, \mathrm{C}_{2} \mathrm{H}_{4}, \mathrm{C}_{2} \mathrm{H}_{6}$ | Lab | Baseline and monthly |
| $\mathrm{NO}_{3}, \mathrm{NO}_{2}, \mathrm{SO}_{4}, \mathrm{Cl}$ | lab | Baseline and monthly |
| Alkalinity | Lab | Baseline and monthly |

## 5. RESULTS

Results from the RABITT field treatability testing at Cape Canaveral Air Station, Naval Air Station Alameda, and Fort Lewis will be presented in the next interim report.

## 6. 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.

## 7. 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 of.

## 8. COSTS

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

## 9. CONCLUSIONS

Two of the five planned RABITT treatability test systems have been installed and are currently being monitored. By the time of the Year 2000 NATO/CCMS meeting, three of the tests should be completed and the final two systems will be operating.

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| Project No. 13 |  |  |  |
| :---: | :---: | :---: | :---: |
| Permeable Reactive Barriers for In Situ Treatment of Chlorinated Solvents |  |  |  |
| Location <br> Dover Air Force Base, Delaware, USA | Project Status Final Report | Media <br> Groundwater | Technology Type In situ abiotic destruction of contaminants |
| Technical Contacts <br> Charles Reeter <br> U.S. Navy <br> $110023^{\text {rd }}$ Ave., Code 412 <br> Port Hueneme, CA 93043 <br> Tel: (805) 982-4991 <br> Fax: (805) 982-4304 <br> E-mail: <br> reetercv@vfesc.navy.mil | Project Dates <br> Accepted 1999 <br> Final Report 2000 | Contaminants <br> Chlorinated solvents: <br> DCE | E, TCE, and cis-1,2- |
| Catherine Vogel <br> DoD SERDP/ESTCP <br> Cleanup Program Manager <br> 901 N. Stuart Street, Suite 303 <br> Arlington, VA 22203 <br> Tel: (703) 696-2118 <br> Fax: (703) 696-2114 <br> E-mail: vogelc @ acq.osd.mil | Costs Documented? Yes, in this report and in more detail in the Final Report (March 2000) | Project Size <br> Field Demonstration <br> Pilot-scale | Results Available? Yes, in this report and in more detail in the Final Report (March 2000) |

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 pretreatment 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 ug ./L of PCE and TCE, $70 \mathrm{ug} / \mathrm{L}$ of cis-1,2 dichloroethene (cis-1,2 DCE), and $2 \mathrm{ug} / \mathrm{L}$ 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 $5 \mathrm{ug} / \mathrm{L}$ of PCE and TCE, $70 \mathrm{ug} / \mathrm{L}$ of cis 1,2-dichloroethene (DCE), and $2 \mathrm{ug} / \mathrm{L}$ 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

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| Project No. 14 |  |  |  |
| :---: | :---: | :---: | :---: |
| Thermal Cleanup Using Dynamic Underground Stripping and Hydrous Pyrolysis/Oxidation |  |  |  |
| Location <br> LLNL Gasoline Spill Site, Livermore, CA. <br> Visalia Pole Yard, Visalia, CA. | Project Status Final Report | Contaminants PAHs, diesel and pentachlorophenol (Visalia) Gasoline (LLNL) (TCE, solvents and fuels at other sites) | Technology Type Dynamic Underground Stripping and Hydrous Pyrolysis/ Oxidation |
| Technical Contacts <br> Robin L. Newmark <br> Lawrence Livermore National <br> Laboratory <br> L-208, P.O. Box 808 <br> Livermore, Ca., 94550 <br> United States <br> Tel: (925)-423-3644 <br> Fax: (925)-422-3925 <br> E-mail: newmark@llnl.gov | Project Dates Accepted 1998 | Media <br> Groundwater and soil |  |
| Paul M. Beam <br> U.S. Department of Energy 19901 Germantown Road Germantown, MD 208741290 <br> United States <br> Tel: 301-903-8133 <br> Fax: 301-903-3877 <br> E-mail: <br> paul.beam@em.doe.gov | Costs Documented? Yes | Project Size <br> Full-scale: <br> Livermore: $100,000 \mathrm{yd}^{3}$ $\left(76,000 \mathrm{~m}^{3}\right)$ <br> Visalia: 4.3 acres, $>130$ <br> ft deep (app. 600,000 m ${ }^{3}$ ) | Results Available? Yes |

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

## 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 ( $30,000 \mathrm{~L}$ ) 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 ( $64,000 \mathrm{~L}$ ) 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 $30 \mathrm{ft}(9 \mathrm{~m})$ 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 $650 \mathrm{ft}(200 \mathrm{~m})$ 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 $2.5 \mathrm{gal} /$ day 9.5 L/day).

## Visalia Pole Yard:

In 1997, DUS and HPO were applied for cleanup of a 4.3 acre ( $17,000 \mathrm{~m}^{2}$ ) 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 ( $150,000-300,000 \mathrm{~L}$ ) of DNAPL product composed of poletreating chemicals (primarily creosote and pentachlorophenol) and an oil-based carrier fluid had penetrated the subsurface to depths of approximately $100 \mathrm{ft}(30 \mathrm{~m}), 40 \mathrm{ft}(12 \mathrm{~m})$ 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 . $(4.5 \mathrm{~kg})$ 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

## 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.

## 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.

## 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.

## 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 $120 \mathrm{ft}(36 \mathrm{~m})$ in diameter and $80 \mathrm{ft}(24 \mathrm{~m})$ high, extending from a depth of $60 \mathrm{ft}(18 \mathrm{~m})$ to a depth of $140 \mathrm{ft}(43 \mathrm{~m})$. The water table is located at $100 \mathrm{ft}(30 \mathrm{~m})$. Due to the presence of relatively thick clay-rich zones, both electrical heating and steam injection were required to heat the target volume.

## 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 $\mathrm{CO}_{2}$, and the distinct isotopic signature of the carbon in the $\mathrm{CO}_{2}$ 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

## LLNL Gasoline Spill Site:

During 21 weeks of thermal treatment operations conducted over about a year, DUS treatment removed more than 7600 gallons ( $29,000 \mathrm{~L}$ ) of an estimated 6200 gallons ( $23,000 \mathrm{~L}$ ) of gasoline trapped in soil both above and below the water table. Prior to thermal treatment, separate phase contamination extended to $>120 \mathrm{ft}(37 \mathrm{~m})$ deep. Approximately $100,000 \mathrm{yd}^{3}\left(76,000 \mathrm{~m}^{3}\right)$ 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 $90^{\circ} \mathrm{C}$. The very positive response of regulators, who provided quick closure authorization for the site, indicates that these methods will be accepted for use.

## 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 $500,000 \mathrm{yd}^{3}\left(380,000 \mathrm{~m}^{3}\right)$ to at least a temperature of $100^{\circ} \mathrm{C}$ by the beginning of August 1997. Uniform heating of both aquifer and aquitard materials was achieved. At this point, about 20,000 gallons $(76,000 \mathrm{~L})$ 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 $300 \mathrm{lb} /$ day $136 \mathrm{~kg} /$ 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 $800 \mathrm{lb} /$ day ( $360 \mathrm{~kg} /$ 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 $960,000 \mathrm{lb}(440,000$ 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 $\mathrm{NO}_{\mathrm{x}}$ 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

## 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.

## 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 $800,000 \mathrm{yd}^{3}\left(600,000 \mathrm{~m}^{3}\right)$ of which about $400,000 \mathrm{yd}^{3}\left(300,000 \mathrm{~m}^{3}\right)$ 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 $\left(\$ 33 / \mathrm{m}^{3}\right)$, 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 $970,000 \mathrm{lb}$. of contaminants was removed or destroyed in about 20 months of operations; previous recovery amounted to $10 \mathrm{lb} /$ 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, $\mathrm{CO}_{2}$ 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 ( $<40 \mathrm{ft}(10 \mathrm{~m})$ ) to relatively deep (>185 ft ( 56 m ) ). In January 1999, steam injection began at a relatively shallow ( $>35 \mathrm{ft}$ ( 11 $\mathrm{m})$ ) site in Ohio in which DNAPL TCE is being removed.

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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 various hole 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 $490,000 \mathrm{ppb}$ at one location and to a non-detect level from up to $12,000 \mathrm{ppb}$ 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 ( $1,1,2,2-\mathrm{TCA}, \mathrm{TCE}, \mathrm{DCE}$ ) at levels up to 260 parts per million ( ppm ). The contamination is 5 to $40 \mathrm{ft}(3.5$ 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 $500 \mathrm{ft}(160 \mathrm{~m})$ 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 dicloromethane (up to $490,000 \mathrm{ppb}$ ), tetrachloroethylene (up to 160 ppb ), trichloroethylene (up to 390 ppb ), trimethylbenzene (up to $2,000 \mathrm{ppb}$ ), and xylenes (up to $2,700 \mathrm{ppb}$ ). 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 semiconfining unit for water and contaminants percolating down toward an unconfined aquifer from 18 to $80 \mathrm{ft}(6$ to 26 m$) \mathrm{bgs}$. This unconfined aquifer is composed primarily of sand and is highly permeable. The top of the aquifer is about $9 \mathrm{ft}(3 \mathrm{~m})$ 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 $2034 \mathrm{~m}^{2}$ and contains 156 viable poplars.
- $1,1,2,2-\mathrm{TCA}$ and TCE are 90 percent of the contaminants (total approximately 260 ppm solvents). USGS estimated 7000 gals/day removal would achieve hydraulic influence.
- 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.


EXPLANATION

- MONITORING WELL: Well number indicates well was sampled throughout the entire location
- MONITORING WELL WITH WATER-LEVEL RECORDER
$\star$ STREAM-STAGE GAGE
+ TENSIOMETER NEST
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 $\mathrm{ft}(1 \mathrm{~m})$, 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 $10 \mathrm{ft}(3 \mathrm{~m})$ apart on the axis running from north to south and $12.5 \mathrm{ft}(4 \mathrm{~m})$ apart on the east-west axis. The trees were planted using a process called deep rooting: $12-\mathrm{ft}$ (4 $\mathrm{m})$ trees were buried nine feet under the ground so that only about 2 to $3 \mathrm{ft}(0.6$ 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

- 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 ( $4,129 \mathrm{~L} /$ day ) and at the end of 30 years are expected to remove approximately 1,999 gallons per day ( $7,528 \mathrm{~L} /$ day).
- Groundwater sampling indicated that the contaminated plume has not migrated off-site during the growing seasons.
- There is no ecological impacts that are attributable to the plantation area. Sampling data have shown non-detectable off-site migration of emissions from transpiration gas.
- Peak transpiration is estimated to occur in approximately 10 to 15 years.
- 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.
- Contaminant uptake is minimal at this time but is expected to improve as the trees mature.
- 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.
- 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 ${ }^{\circledR}$ 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, 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 ${ }^{\circledR}$ 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, indicate 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 $615 \mathrm{ppb}, 12,000 \mathrm{ppb}$ 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 $2 \mathrm{ppb}, 246$ 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 $8 \mathrm{ppb} / \mathrm{v}$ ) 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 $17 \mathrm{ft}(22 \mathrm{~m})$ 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: $288 \mathrm{~g} / \mathrm{m}^{2}$ for whips compared to $273 \mathrm{~g} / \mathrm{m}^{2}$ for caliper trees in the $<0.5 \mathrm{~mm}$ range; $30 \mathrm{~g} / \mathrm{m}^{2}$ for whips compared to $36 \mathrm{~g} / \mathrm{m}^{2}$ for the caliper trees in the 0.5 to 1.0 mm range; and $60 \mathrm{~g} / \mathrm{m}^{2}$ for the whips compared to $91 \mathrm{~g} / \mathrm{m}^{2}$ 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 sitespecific 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 the to volumetric flux of groundwater through a site. The horizontal hydraulic conductivity at the demonstration site in Fort Worth, Texas is approximately $6 \mathrm{~m} /$ 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 $1 \mathrm{ft}^{3} / \mathrm{sec}$ or $3 \mathrm{~cm}^{3} / \mathrm{sec}$ ) 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 $0.049 \pm 0.02$ 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 $4.5 \mathrm{mg} / \mathrm{L}$ in water from all upgradient wells and one well between the tree plantations (well 522). Whereas, they were below $3.5 \mathrm{mg} / \mathrm{L}$ 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 $1.76 \mathrm{mg} / \mathrm{L}$. The dissolved oxygen concentration in several wells beneath the planted trees was less than $1 \mathrm{mg} / \mathrm{L}$. 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: $\quad \$ 65,700$
Maintenance $\$ 15,300$
Total: $\$ 105,000$
1997 maintenance: $\quad \$ 26,000$
1998 maintenance: $\quad \$ 14,000$ (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: $\quad \$ 10,000$
Site work
Monitoring (research level) well installation: \$90,000

Development of Plantations -1 acre (includes landscaping costs): $\$ 41,000$
Weather Station: \$ 3,100
Survey: $\quad \$ 25,000$
Purchase of Trees
Whips (\$0.20 each): \$100
Five-gallon buckets (\$18 each): \$2,000
Installation of Irrigation System: $\quad \$ 10,000$
Yearly O\&M
Landscaping: $\quad \$ 2,000$
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 Interim | Media <br> Groundwater | Technology Type In-situ bioremediation (reactive zone or biobarrier) |
| Technical Contact <br> Dr. Ludo Diels <br> Dr. Leen Bastiaens <br> Dr. D. van der Lelie <br> Flemish Institute for <br> Technological Research (Vito) <br> Boeretang 200 | Project Dates <br> Accepted 1999 <br> Final report 2002 | Contaminants <br> Heavy metals (zinc, cadmium, arsenic, lead, chromium, nickel, copper) sulfate |  |
| Belgium <br> Tel: +32 14335100 <br> Fax: +32 14580523 | 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 metal refining, metal processing, and surface treatment industries. Immobilization followed by phytostabilization 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 already has 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 groundwatercontaining heavy metals. Through stimulation of sulfate 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 two different industrial sites in Belgium. Insitu 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 ( $10-150 \mathrm{mg} / \mathrm{l}$ ), cadmium ( $0.4-4 \mathrm{mg} / \mathrm{l}$ ) and arsenic (20-270 $\mu \mathrm{g} / \mathrm{l}$ ) are present in the groundwater. Also relatively high concentrations of sulfate (400$700 \mathrm{mg} / \mathrm{l}$ ) were measured, which is favorable for SRB-activities. Groundwater samples taken further away from the source have lower metals and sulfate concentrations.

Industrial site 2 (surface treatment) has serious chromium (up to $8300 \mu \mathrm{~g} / \mathrm{l}$ ), zinc (up to $78 \mathrm{mg} / \mathrm{l}$ ), lead (up to $72 \mu \mathrm{~g} / \mathrm{l}$ ), nickel ( $u$ to to $3500 \mu \mathrm{~g} / \mathrm{l}$ ), copper ( $92 \mathrm{mg} / \mathrm{l}$ ), and cadmium (up to $17 \mathrm{mg} / \mathrm{l}$ ) problems in the groundwater. Very high sulfate (up to $3000 \mathrm{mg} / \mathrm{l}$ ) concentrations are also present. This groundwater has also a very low pH (between 2 and 4).

## 3. DESCRIPTION OF THE PROCESS

## Bioprecipitation process:

In-situ precipitation of heavy metals and sulfates 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 sulfates to sulfites and further to sulfides, which then form stable and rather insoluble metal sulfides:

$$
\begin{gathered}
\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{SO}_{4}{ }^{2-}==>2 \mathrm{HCO}_{3}^{-}+\mathrm{HS}^{-}+\mathrm{H}^{+} \\
\mathrm{H}_{2} \mathrm{~S}+\mathrm{Me}^{++}==>\underline{\mathrm{MeS}}+2 \mathrm{H}^{+}
\end{gathered}
$$

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

- $\quad$ Sulfate reducing bacteria (SRBs) must be present in the aquifer. In case no SRBs are present among the autochthonous micro-population in the aquifer, appropriate microorganisms have to be introduced in the aquifer.
- Sulfate should be available. 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 $\left(\mathrm{E}_{\mathrm{h}}\right)$ is necessary.

The applicability of in-situ bioprecipitation of heavy metals on sites should therefore 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, sulfate requirements, influence of temperature, etc.
- 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 sulfides will be checked.
- Further is clogging due to biomass production and metal precipitates an important issue that has to be evaluated.

3. Field demonstration 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 the carbon source (no explosion danger like methanol, not contaminated by other impurities like molasses). 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 $\mathrm{HgCl}_{2}$ ), nearly no Zn removal could be obtained. The addition of a low concentration of acetate leads to a reduction of Zn from $10700 \mu \mathrm{~g} / \mathrm{l}$ to $213 \mu \mathrm{~g} / \mathrm{l}$. In the same groundwater, As and Cd also were 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, 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 sulfate concentrations were also quite low and this showed not to be favorable for the SRB-bacteria. Only in the case of added SRBs could the metals be removed.

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

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

At the second test site, the sulfate concentrations were quite low ( $\left.200 \mathrm{mg} \mathrm{SO}_{4}{ }^{2-} / \mathrm{l}\right)$. Only after the addition of extra sulfate ( $2000 \mathrm{mg} \mathrm{SO}_{4}{ }^{2-} / \mathrm{ll}$ ) or of zero valent iron could the redox 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 $\mathrm{HgCl}_{2}$ ) did not lead to metal removal. Also $\mathrm{Pb}, \mathrm{Zn}, \mathrm{Cr}$, 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 | 201 | 203 | 181 | 235 | 247 |
|  | mV | mV | mV | mV | mV | mV |
| R2: aquifer $+\mathrm{GW}+\mathrm{HgCl}_{2}$ | 325 | 316 | 341 | 309 | 315 | 301 |
|  | mV | mV | mV | mV | mV | mV |
| R3: aquifer + GW + K-acetate | 175 | 173 | 132 | 159 | 198 | 143 |
|  | mV | mV | mV | mV | mV | mV |
| R4: aquifer + GW + K-acetate + Dd8301 | 229 | 197 | 290 | 250 | 145 | 142 |
|  | mV | mV | mV | mV | mV | mV |
| R5: aquifer + GW + Postgate C + K-acetate | 88 mV | 44 mV | -308 | -322 | -284 | -316 |
| + Dd8301 | 88 mV | 44 mV | mV | mV | mV | mV |
| R6: Aquifer $+\mathrm{GW}+\mathrm{Fe} 44$ | 221 | 144 |  | 32 | 143 | 73 mV |
|  | mV | mV | 6 mV | mV | mV | 73 mV |
| R7: aquifer $+\mathrm{GW}+\mathrm{HgCl}_{2}+\mathrm{FeA} 4$ | 303 | 278 | -212 | -208 | -168 | -88 mV |
|  | mV | mV | mV | mV | mV |  |
| R8: aquifer $+\mathrm{GW}+\mathrm{K}$-acetate +Fe A 4 | 138 | -129 | -402 | -189 | -460 | -380 |
|  | mV | mV | mV | mV | mV | mV |
| R9: aquifer + GW + K-acetate + FeA4 + | 106 | -398 | -246 | -229 | -241 | -198 |
| Dd8301 | mV | mV | mV | mV | mV | mV |

NOTES: 5 ml K-acetate (25\%); Postgate C 10X concentrated; $10 \mathrm{~g} \mathrm{FeA4}$;
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 |  |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Total | Sol. | Total | Sol. | Total | Sol. | Total | Sol. | Total | Sol. |
| R1: aquifer + GW | 62 | 54 | 52 | 45 | 80 | 81 | 56 | 53 | 65 | 74 |
| R2: aquifer + GW + HgCl 22 | 54 | 45 | 44 | 42 | 68 | 70 | 93 | 63 | 69 | 74 |
| R3: aquifer + GW + K- <br> acetate | 62 | 52 | 45 | 51 | 62 | 66 | 33 | 28 | 73 | 16 |
| R4: aquifer + GW + K- <br> acetate + Dd8301 | 37 | 34 | 54 | 60 | 100 | 86 | 65 | 70 | 78 | 74 |
| R5: aquifer + GW + Postgate <br> C + K-acetate + Dd8301 | 424 | 82 | 270 | 103 | 3.2 | 0.65 | 3.4 | $<2.5$ | 22 | 1.1 |
| R6: aquifer + GW + FeA4 | 57 | 51 | 51 | 34 | 1.2 | 1.2 | 6.7 | 2.8 | 3.1 | 2.2 |
| R7: aquifer + GW + HgCl <br> FeA4 | 65 | 51 | 72 | 63 | 6.5 | 1.0 | 16 | 2.8 | 7.5 | 1.2 |
| R8: aquifer + GW + K- <br> acetate + FeA4 | 48 | 33 | 28 | $<20$ | 1.3 | 1.9 | 4.6 | $<2.5$ | 3.9 | 1.9 |
| R9: aquifer + GW + K- <br> acetate + FeA4 + 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; $10 \mathrm{~g} \mathrm{FeA4;} \mathrm{Concentrations} \mathrm{below} \mathrm{the} \mathrm{remediation} \mathrm{standard} \mathrm{(20}$ $\mu \mathrm{g} / \mathrm{l}$ ) 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 the determination of the kinetics of the remediation system, which is necessary for the optimal design of the pilot project in the field. The results will be presented in the next interim report.

## 5. HEALTH AND SAFETY

For safety reasons, no methanol was used and all the tests were performed with acetate as the electron donor. The study must now show that the use of acetate is an applicable alternative.

## 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. CONCLUSIONS

The batch tests showed for both sites the feasibility of metals removal from groundwater by the induction in situ bioprecipitation. However it took quite long times before the redox potential dropped to below 220 mV . This indicates that a long lag period will be necessary and, at the moment, no information is available about the kinetics. Therefore, both projects will continue by starting experiments under the most optimal conditions. These tests will allow the determination of the kinetics of the remediation system, which is necessary for the optimal design of the pilot project in the field. The results will be presented in the next interim report.

## 8. 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 pp.150-155.
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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 New Project | Media <br> Soil and groundwater | Technology Type Excavation and treatment of waste |
| Technical Contact <br> René Goubier <br> ADEME <br> BP 406 | $\begin{array}{\|l\|} \hline \text { Project Dates } \\ 06 / 1999 \\ 07 / 2002 \\ \hline \end{array}$ | Contaminants <br> Complex contamination: solvents (BTEX and chlorinated); PCBs; phénols, phthalates; Pb , Zn |  |
|  | Project Size Full-scale |  |  |

Please note that this project summary was not updated since the 1999 Annual Report.

## 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 important quantity of drums were 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: 3700 drums were excavated and treated and 14,000 tons of polluted soil was confined on the site. The treatment of this polluted soil is carried out at the present time by solvent washing. The total cost of these first phases of clean up is about 65 millions francs.

## 2. THE NEW PROJECT

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:

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

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 will be:

- to improve the knowledge of the contamination source and to prepare the clean up of the remaining hot spots
- to 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. 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 <br> New project | Contaminants <br> Complex <br> contamination, <br> chlorobenzene | Technology Type <br> 9 different types of <br> biotic and abiotic <br> technologies |
| Technical Contact <br> Dr. Holger Weiss <br> UFZ-Centre for Environmental <br> Research <br> Permoserstrasse 15 <br> D-04318 Leipzig <br> Germany | Project Dates <br> $7 / 1999-6 / 2002$ | Media <br> Groundwater |  |
|  | Costs Documented? <br> Yes | Project Size <br> Pilot-scale | Results Available? <br> Not yet |

Please note that this project summary was not updated since the 1999 Annual Report.

## 1. INTRODUCTION

The aim of the SAFIRA project is the examination and further development of in situ groundwater decontamination technologies. A site near Bitterfeld (Germany) was selected as a model location. Different types of technologies (e.g., catalytic, microbial, sorption) have to prove their performance and long term stability under the real-world conditions of an in situ pilot plant. It is a cooperation project between UFZ Center for Environmental Research Leipzig-Halle, TNO (The Netherlands) and the universities Dresden, Halle, Kiel, Leipzig, and Tuebingen.

## 2. BACKGROUND

The region of Bitterfeld was selected as the model location for investigations into developing powerful in situ technologies for the remediation of complexly contaminated groundwater. The soil and water environmental compartments in the Bitterfeld/Wolfen district have suffered sustained damage as a result of over a century of lignite-mining and chemical industry. Whereas relevant soil pollution is mainly confined to industrial locations (plant sites) and landfills, the persistent penetration of the groundwater by pollutants has resulted in contamination attaining a regional scale. Consequently, an area of about $25 \mathrm{~km}^{2}$ with an estimated volume of some 200 million $\mathrm{m}^{3}$ is now partly highly polluted and must be regarded as an independent source of contamination. This pollution is characterised by the extensive distribution of halogenised hydrocarbons, especially chlorinated aliphatics and chlorinated aromatics.

## 3. TECHNICAL CONCEPT

Technology developed and tested in laboratories will be scaled up in two stages: a mobile test unit and an in situ pilot plant. A mobile decontamination unit has been designed for this purpose as a "window in the aquifer". Groundwater from a depth of about 20 m is pumped into a storage tank without coming into contact with oxygen. This polluted water will then be used to charge five possible test columns with the physico-chemical conditions of the aquifer being preserved.

The methods tested successfully in the laboratory and in the mobile decontamination unit have to prove their chemical and hydrological long-term stability and will be optimised in a pilot plant. Five shafts with a depth of about 22.5 m and an inner diameter of 3 m were constructed. Several experimental columns of up to 1.4 m in diameter will be installed into these shafts and will be supplied with the contaminated groundwater directly from the aquifer. The contaminated water will vertically flow through the reactors and will be cleaned. Numerous sampling and process controlling facilities as well as a variable design of the reaction columns will enable the analyses of relevant chemical and hydraulic processes during
operation and competitive development in technology under real-world conditions. The technologies tested in the first phase of the pilot plant are:

- anaerobic microbial degradation of the contaminants
- aerobic microbial degradation
- electrocatalytical dehalogenation
- zeolith supported catalysts
- oxidizing catalysts
- sorption barriers
- redox reactors
- microbial degradation in combination of adsorption onto several high porosity media
- bioscreens

The assessment of the different techniques will follow chemical, ecotoxicological, economic and environmental criteria.

## 4. ANALYTICAL APPROACH

A weekly sampling of the inflow and outflow of every reactor will occur. All samples will be analyzed in the laboratory at the site. Regular analyses will include a GC analyses (TCE, DCE, dichlorobenzene, chlorobenzene, benzene), ion-chromatography (chloride, sulfate, phosphate, nitrate), TOC, and AOX. Additional samplings and analysis of water and solid material are optional.

## 5. RESULTS

First results of the experiments in the laboratory and in the mobile test unit are summarized in reports (see references).

## 6. HEALTH AND SAFETY

The shafts will ventilated before the staff enter the shafts for sampling. The German regulations for safety have to be followed. The shafts are equipped with warning systems for fire, gas, water, pressure in the reactors, temperature, air quality and controlling the pumps. Most of this equipment is only be necessary for research purpose.

## 7. ENVIRONMENTAL IMPACTS

The outflow water of the different reactors is cleaned additionally in a cleaning facility. This option was necessary only for the pilot plant to demonstrate the technologies and to avoid environmental impact. The hydrologic regime is not disturbed. Monitoring wells are installed around the shafts.

## 8. COSTS

Not yet available.

## 9. CONCLUSIONS

Not yet available.

## 10. REFERENCES

Weiss H., Teutsch G., Daus B. (ed.)(1997): Sanierungsforschung in regional kontaminierten Aquiferen (SAFIRA) - Bericht zur Machbarkeitsstudie für den Modellstandort Bitterfeld.-UFZ-Bericht 27/1997, Leipzig

Weiss H., Daus B., Fritz P., Kopinke, F.-D., Popp, P. \& Wünsche, L. (1998): In situ groundwater remediation research in the Bitterfeld region in eastern Germany (SAFIRA); In: M. Herbert \& K. Kovar (Ed.): Groundwater Quality: Remediation and Protection.- IAHS Publication no. 250, 443-450.

| Project No. 19 |  |  |  |
| :---: | :---: | :---: | :---: |
| Succesive Extraction-Decontamination of Leather Tanning Waste Deposited Soil |  |  |  |
| Location <br> University of Istanbul | Project Dates Accepted 1998 Final Report 2001 | Report Status Interim | Contaminants Organic and inorganic |
| Technical Contact <br> Dr. Erol Erçag University of Istanbul Faculty of Engineering, Department of Chemistry Avcilar, 34850 Istanbul, Turkey Tel: 021259384 7, Ext. 1191 <br> Fax: 02125911998 <br> Ercag@istanbul.edu.tr | Costs Documented? No | Results Available None | Project Size Laboratory/field |

## 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

Insufficient data to draw any meaningful conclusions.

## 7. REFERENCES

Not applicable.

| Project No. 20 |  |  |  |
| :---: | :---: | :---: | :---: |
| Interagency DNAPL Consortium Side-by-Side Technology Demonstrations at Cape Canaveral, Florida |  |  |  |
| Location | Project Status | Contaminants | Technology Type |
| $\begin{aligned} & \text { Cape Canaveral, FL, } \\ & \text { USA } \end{aligned}$ | Ongoing/Interim | DNAPL | 3 Technologies Side-by-Side |
| Technical Contact | Project Dates | Media |  |
| Tom Early | 1999-2001 | Soil and Grou |  |
| Oak Ridge National |  |  |  |
| Laboratory |  |  |  |
| P.O. Box 2008 |  |  |  |
| Oak Ridge, TN 37831- |  |  |  |
| 6038 | Costs Documented? | Project Size | Results Available? |
| Tel: 865/576-2103 | 2001 | 2 Acres | 2001 |
| Fax: 865/574-7420 |  |  |  |

## 1. INTRODUCTION

An important step in reducing technology risk and increasing user and regulatory acceptance of DNAPL remediation, characterization and monitoring technologies involves conducting concurrent, "side-by-side" field demonstrations. These side-by-side" demonstrations result in comparative cost and performance data collected under the same field conditions. Through appropriate documentation, the resulting cost and performance data can be evaluated for site-specific applications. Side-by-side demonstrations help to fill an important "gap" in the process of technology development and deployment and will accelerate technology privatization.

## 2. BACKGROUND

Dense non-aqueous phase liquids (DNAPLs) pose serious, long-term ground water contamination problems due to their toxicity; limited solubility in ground water; and significant migration potential in soil gas, ground water, 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 ground water contamination. Many agency and private-sector sites have DNAPL contamination problems, including federal, state, and local government agencies. The Office of Management and Budget estimates that the federal government alone will spend billions of dollars for environmental clean up of DNAPL contamination problems.

While various DNAPL remediation, characterization and monitoring technologies have been demonstrated in the past, it is difficult, if not impossible, to make meaningful comparisons of either performance or cost among these technologies because of the variable conditions at the demonstration sites. As a result, "problem holders" and regulatory officials have been reluctant to deploy these technologies for site clean up. In order to expedite the regulatory acceptance and use of these innovative remedial technologies, comparative cost and performance data must be collected.

## 3. TECHNICAL CONCEPT

In 1998, a multiagency consortium was organized by the United States Department of Energy/Office of Environmental Management (DOE/EM) and the Department of Defense (DOD) through the Air Force Research Laboratory (AFRL) in cooperation with the 45th space wing, the National Aeronautics and Space Administration (NASA) and the United States Environmental Protection Agency (EPA) to demonstrate innovative DNAPL remediation and characterization technologies at a NASA remediation
site on Cape Canaveral Air Station, Cape Canaveral, FL. This Interagency DNAPL Consortium (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);
- cost-share the demonstration and comparison of these remediation and monitoring system technologies;
- 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 addition to ex situ treatment and disposal.

In order to conduct this side-by-side demonstration, an IDC Core Management Team was organized. The IDC consists 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 utilizes a Technical Advisory Group (TAG) for support in making decisions that concern individual evaluation of remediation systems. The IDC TAG is comprised of experts from industry, academia and federal agencies. With the support of the TAG, the Team selected three of the most promising remediation technologies for deployment and evaluation at Launch Complex 34.

## 4. ANALYTICAL APPROACH

## In Situ Chemical Oxidation

In situ oxidation using potassium permanganate is a potentially fast and low cost solution for the destruction of chlorinated ethylenes (TCE, PCE, etc), 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, perchloroethylene, dichloroethylene isomers, and vinyl chloride. It is effective for the remediation of DNAPL, absorbed phase and dissolved phase contaminants and produces innocuous breakdown products such as carbon dioxide, chloride ions and manganese dioxide. The permanganate solution typically is applied at concentrations of one to three percent solution via injection wells. This solution is easily handled, mixed and injected and is non-toxic and non-hazardous.

Bench-scale laboratory tests of potassium permanganate with trichloroethylene have resulted in up to a $90 \%$ reduction of trichloroethylene 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.

## Benefits

- Chemically oxidizes a wide range of organic compounds to innocuous end-products over a wide pH range
- Visible (purple) solution makes it easy to track the injection influence or the degree of treatment
- Chemically stable in water (very slow auto-degradation)-stays in solution until it is reacted
- $\quad$ No off-gas treatment required


## Six Phase Soil Heating

The Six Phase Soil Heating technology removes contaminants from soil and ground water by passing an electrical current through the soil matrix. The passage of current generates heat due to electrical resistance within the soil. This is the same process used in any electrically heated device (e.g., clothes iron, heater, stove). Heat is generated throughout the soil in the remediation area and the temperature of the soil is increased to the boiling point of water. Soil moisture becomes steam that is captured by vapor recovery wells for removal. Soil contaminants are vaporized concurrently and are captured for ex situ treatment.

## Benefits

- Heat is generated uniformly throughout the treatment volume. While low permeability lenses reduce the performance of other technologies that rely on the vertical movement of a fluid or vapor though the soil matrix, soil heterogeneity or low permeability does not adversely effect Six Phase Soil Heating. In fact, low permeability soils tend to carry greater current than do sandy soils, thus, become hotter, and boil constituents faster.
- Anaerobic dechlorination of solvents will add conductive chloride ions to "hot spots", likewise attracting current for faster remediation of the impacted regions of the site.
- The boiling of soil moisture in clay lenses forms steam to "sweep out" volatile organic compounds. This steam stripping process effectively increases the permeability clay soils.
- Because Six Phase Soil Heating treats all soils in the treatment volume, there are no untreated regions from which contaminants could diffuse later and cause rebound. Rebound has not been observed at any Six Phase Soil Heating site.
- The presence of perched water does not reduce the effectiveness of Six Phase Soil Heating.


## In Situ Thermal Remediation (Steam Injection)

Thermal remediation by steam injection and recovery uses Dynamic Underground Stripping, Steam Enhanced Extraction, Hydrous Pyrolysis/Oxidation, and Electrical Resistance Tomography. Combining these technologies the Dynamic Underground Stripping System uses boilers to generate steam which is then pumped into injection wells that surround the contaminants. The steam front volatilizes and mobilizes the contaminants as it pushes the resulting steam front toward a central network extraction well where it is vacuumed to the surface. Direct electrical heating of soils, clay and fine-grained sediments causes trapped water and contaminants to vaporize and forces them into steam zones where vacuum extraction removes them. Electrical Resistance Tomography is used as a process control method to measure electric resistance and temperatures in the subsurface that allow for real-time control of the heating process.

## Benefits

- Faster clean-up, potential closure within months to years, not decades
- Removes source contaminants effectively
- Treats contamination both above and below the water table, with no practical depth limitation


## 5. RESULTS

In situ chemical oxidation and six phase heating technologies were implemented in 2000 on the two outside plots of the three plots in the study. Steam stripping will be initiated in January 2001. Preliminary data from the first two demonstrations are being analyzed. Complete results will be presented at the September 2000 Pilot Study meeting in Belgium.

## 6. HEALTH AND SAFETY

To be determined.

## 7. ENVIRONMENTAL IMPACTS

To be determined.

## 8. COSTS

To be determined.

## 9. CONCLUSIONS

To be determined.

| Project No. 21 |  |  |  |
| :---: | :---: | :---: | :---: |
| Development and Use of a Permeable Adsorptive Reactive Barrier System for Ground Water Cleanup at a Chromium-Contaminated Site |  |  |  |
| Location <br> Wood impregnation plant Leisi, Willisau, canton Luzern, Switzerland | Project Status New | $\begin{aligned} & \text { Contaminants } \\ & \text { Chromium (CrVI) } \end{aligned}$ | Technology Type <br> Permeable reactive <br> wall |
| Technical Contact <br> Prof. Rita Hermanns Stengele Institute of Geotechnical Engineering <br> Swiss Federal Institute of Technology Zurich CH-8093 Zurich, Switzerland Tel: +41-1-6662524 | Project Dates <br> Accepted 2000 | Media <br> Ground water |  |
| Fax: +41-1-6331248 <br> E-mail: <br> hermanns@igt.baug.ethz.ch | Costs Documented? <br> Yes (estimated) | Project Size Full-scale | Results Available? No |

## 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 $20^{\text {th }}$ century. It is located in the small village of Willisau in the canton of Luzern, Switzerland. The area is about $20,000 \mathrm{~m}^{2}$. 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 $\mathrm{k}_{\mathrm{f}} \approx 10^{-3}-10^{-4} \mathrm{~m} / \mathrm{s}$.

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 byproducts.

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 (longterm 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, timesettlement 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 Using Steam Injection |  |  |  |
| Location <br> Former hazardous waste disposal site, Mühlacker, Germany | Project Status New project | Contaminants TCE, BTEX | Technology Type Steam injection |
| Technical Contact Dr. H.-P. Koschitzky Research Facility for Subsurface Remediation, VEGAS, University of Stuttgart, Pfaffenwaldring 61 | $\begin{aligned} & \hline \text { Project Dates } \\ & \text { July } 1999 \text { - January } \\ & 2001 \end{aligned}$ | Media <br> Unsaturated zone |  |
| D-70569 Stuttgart, Germany koschi@iws.uni-stuttgart.de | Costs Documented? Not yet | Project Size Pilot-scale | Results Available? Not yet |

## 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 subsurface 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 the technology is currently 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. Detailed site investigation led 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 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 is approximately $3000 \mathrm{~m}^{3}$.

The pilot plant is operated by two companies: Züblin Umwelttechnik GmbH and Preussag Wassertechnik GmbH and $V E G A S$ from the University of Stuttgart who conducts the scientific oversight. The pilot study is 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 has a diameter of about 20 m and consists of one central steam injection well surrounded by six extraction wells. The extraction wells can be used simultaneously for vapour and liquid extraction. All wells reach to a depth of 16 m below ground surface and are screened from 7 m to 15 m . Steam is generated using a gas-fired 110 kW steam generator. Extracted gases are passed through a condenser. Incondensable gases flow through a catalytic combustion unit before being vented to the surrounding atmosphere. Condensate flows in liquid separators where the contaminant is separated from the water. Liquids are removed from the wells with surge pumps, passed through a cooler, and flow in a separator where the non-aqueous phase is separated from the water.

In order to measure temperatures in the subsurface up to a depth of 15 m , ten temperature monitoring lances with a total of 100 sensors were installed at spaces every 70 cm of depth. Detailed monitoring of gas and liquid flow rates and temperatures is carried out during the pilot test.

## 4. ANALYTICAL APPROACH

Soil samples were taken and analyzed to determine the extent 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 are measured weekly in the extracted vapours and liquids using GC and HPLC methods and a flame ionization detector (FID).

## 5. RESULTS

First results of the pilot test can be found in Theurer et al. (2000).

## 6. HEALTH AND SAFETY

Safety equipment is used by the staff according to German safety regulations. The pilot plant is equipped with warning systems to control vapour and liquid streams, temperatures, and performance of the pumps.

## 7. ENVIRONMENTAL IMPACTS

Extracted vapours and liquids are cleaned on-site in a treatment facility consisting of a catalytic combustion unit and stripping columns. Thus, emissions to the environment are avoided. Measures for protection against noise are undertaken. Monitoring wells were installed to control contaminant concentrations in the underlying aquifer.

## 8. COSTS

Not yet available.

## 9. CONCLUSIONS

Not yet available.

## 10. REFERENCES

1. 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.
2. 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).

| Project No. 23 |  |  |  |
| :---: | :---: | :---: | :---: |
| Bioremediation of Pesticides |  |  |  |
| Location <br> Stauffer Management Company Superfund Site, Tampa, FL | Project Status <br> New project | Contaminants Chlordane, DDT, DDD, DDE, dieldrin, molinate, toxaphene | Technology Type Composting process (Xenorem ${ }^{\mathrm{TM}}$ ) |
| Technical Contact Brad Jackson U.S. EPA, Region 4 | Project Dates <br> Accepted 2000 <br> Final Report 2001 | Media Soil |  |
| 61 Forsyth Street, SW <br> Atlanta, GA 30303-8960 <br> Tel: 404-562-8925 <br> Fax: 404-562-8896 <br> E-mail: jackson.brad@epa.gov | Costs Documented? <br> Yes - Field <br> Demonstration | Project Size <br> Field Demonstration: 500 <br> $y^{3}{ }^{3}$ <br> Full-Scale: $16,000 \mathrm{yd}^{3}$ | Results Available? <br> Yes - Field <br> Demonstration <br> Soon - Full-Scale |

## 1. INTRODUCTION

The Stauffer Management Company (SMC) 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 has shown concentration reductions of more than 90 percent for DDD and nearly 90 percent reduction for chlordane. Beginning in May 2000, the project has been operating under full-scale conditions. The full-scale remediation is expected to be completed by 2002.

## 2. BACKGROUND

Located in Tampa, Florida, the SMC site manufactured and distributed agricultural chemical products (organochlorine and organophosphorus 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. Typical pesticide concentrations measured in the soil were chlordane ( $47.5 \mathrm{mg} / \mathrm{kg}$ ), DDD ( $162.5 \mathrm{mg} / \mathrm{kg}$ ), DDE ( $11.3 \mathrm{mg} / \mathrm{kg}$ ), DDT ( 88.4 $\mathrm{mg} / \mathrm{kg}$ ), dieldrin ( $3.1 \mathrm{mg} / \mathrm{kg}$ ), molinate ( $10.2 \mathrm{mg} / \mathrm{kg}$ ), and toxaphene ( $469 \mathrm{mg} / \mathrm{kg}$ ).

The site received final status under the Superfund program in 1996. Thermal desorption was initially chosen as the remedial option. However, due to 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. If these objectives were met, full-scale deployment of the technology would ensue to treat $16,000 \mathrm{yd}^{3}$ of pesticide contaminated soil.

## 3. TECHNICAL CONCEPT

AstraZeneca Group PLC, the affiliate of SMC, developed a patented composting process called Xenorem ${ }^{\text {TM }}$ for remediating soils contaminated with pesticides. Xenorem ${ }^{\text {TM }}$ uses anaerobic and aerobic cycles to bioremediate pesticides with indigenous bacteria and addition of amendments.

Using $500 \mathrm{yd}^{3}$ of excavated soil from "hot spots" at the site, a field demonstration was conducted in an enclosed on-site warehouse from June 1997 until September 1998. Soil amendments, including organic wastes or byproducts (cow manure and straw), were added to the compost pile to maintain desired
conditions of temperature, oxygen, pH and nutrient availability. The addition of amendments took place initially and at several intervals throughout the length of the project. The total volume of the compost pile reached $1,193 \mathrm{yd}^{3}$ at the conclusion of the demonstration. The process used an initial aerobic environment with high levels of nutrients, followed by an anaerobic cycle when the pile was covered with a tarp. The demonstration was conducted during hot and cold weather periods and used to assess amendment quality effects and use of various mixing equipment.

## 4. ANALYTICAL APPROACH

Standard operating procedures were performed for soil sampling and collection of composite samples.

## 5. RESULTS

Table 1 shows the cleanup levels specified for selected constituents, the initial $\left(\mathrm{T}_{0}\right)$ and end ( $\mathrm{T}_{64}$ ) concentrations for the field demonstration, and the percent reduction in concentration over that period.

Table 1: Concentrations of Selected Contaminants during the SMC Field Demonstration

| Contaminant | Cleanup Level <br> $(\mathbf{m g} / \mathbf{k g})$ | $\mathbf{T}_{\mathbf{0}}$ Concentration <br> $(\mathbf{m g} / \mathbf{k g})$ | $\mathbf{T}_{\mathbf{6 4}}$ Concentration <br> $(\mathbf{m g} / \mathbf{k g})$ | Reduction in <br> Concentration (\%) |
| :--- | :--- | :--- | :--- | :--- |
| Chlordane | 2.3 | 47.5 | 5.2 | 89 |
| DDD | 12.6 | $242^{*}$ | 23.1 | 90.5 |
| DDE | 8.91 | 11.3 | 6.8 | 40 |
| DDT | 8.91 | 1.4 | 98 |  |
| Dieldrin | 0.19 | 3.1 | BDL | NA |
| Toxaphene | 2.75 | 469 | 29 | 94 |
| Molinate | 0.74 | 10.2 | NA |  |

* Consists of original DDD value ( $162.5 \mathrm{mg} / \mathrm{kg}$ ), plus the amount converted from DDT in the first few weeks of treatment, NA - Not Applicable, BDL - Below Detection Limit


## 6. HEALTH AND SAFETY

Not Available.

## 7. ENVIRONMENTAL IMPACTS

Not Available.

## 8. COSTS

Although specific costs are not available for the field demonstration, the vendor provided typical costs for a cleanup using the Xenorem ${ }^{\text {TM }}$ process. Total project costs were estimated at $\$ 192 / \mathrm{yd}^{3}$, including $\$ 132 / \mathrm{yd}^{3}$ for treatment using Xenorem ${ }^{\mathrm{TM}}$ and $\$ 50 / \mathrm{yd}^{3}$ for non-technology expenses such as soil excavation costs.

## 9. CONCLUSIONS

Based on the results from the field demonstration, the Xenorem ${ }^{\mathrm{TM}}$ technology is being deployed at fullscale at the SMC site to treat approximately $16,000 \mathrm{yd}^{3}$ of soil. The initial full-scale operation entails treating $4,000 \mathrm{yd}^{3}$ batches of contaminated soil. The field demonstration also has established amendment quality specifications for full-scale use, along with experience on a broader range of amendment types.

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| Project No. 24 |  |  |  |
| :---: | :---: | :---: | :---: |
| Surfactant-Enhanced Aquifer Remediation |  |  |  |
| Location <br> Marine Corps Base, Camp Lejeune, NC | Project Status <br> New project | Contaminants tetrachloroethylene (PCE) | Technology Type Surfactant flushing |
| Technical Contact <br> Laura Yeh <br> Naval Facilities Engineering <br> Service Center <br> 560 Center Drive <br> Port Hueneme, CA 93043 <br> Tel: 805-982-1660 <br> Fax: 805-982-1592 <br> E-mail: yehsl@nfesc.navy.mil <br> Leland M. Vane, Ph.D. <br> U.S. EPA <br> National Risk Management <br> Research Laboratory <br> 26 W. Martin Luther King Dr. <br> Cincinnati, OH 45268 <br> Tel: 519-569-7799 <br> Fax: 513-569-7677 <br> E-mail: vane.leland@epa.gov <br> Gary A. Pope, Ph.D. <br> The University of Texas <br> Austin, TX 78712 <br> Tel: 512-471-3235 <br> Fax: 512-471-3605 <br> E-mail: <br> gary_pope@pe.utexas.edu | Project Dates <br> Accepted 2000 <br> Final Report 2001 | Media <br> Groundwater |  |
| Frederick J. Holzmer |  |  |  |
| Duke Engineering \& Services 4433 NW Seneca Ct. <br> Camas, WA 98607 <br> Tel: 360-834-6352 <br> Fax: 360-834-7003 <br> E-mail: <br> fiholzme @ dukeengineering.c om | Costs Documented? <br> Yes - Under <br> Review | Project Size <br> Field Demonstration (wellfield size of 20 feet by 30 feet) | Results Available? Yes |

## 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, NC. 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 1454 -PO sulfate ${ }^{\mathrm{TM}}$, 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 in the extraction well effluent from 1.1 to 5 percent by weight ( $\mathrm{wt} \%$ ), slightly above the reinjection concentration of $4 \mathrm{wt} \%$. 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 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 $29 \pm 7$ 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 $1 \times 10^{-4}$ to $5 \times 10^{-4} \mathrm{~cm} / \mathrm{sec}(0.28-1.4 \mathrm{ft} / \mathrm{day})$, whereas K in the basal silt is estimated to be as low as about $1 \times 10^{-5}$ to $1 \times 10^{-4} \mathrm{~cm} / \mathrm{sec}(0.028-0.28 \mathrm{ft} /$ 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.

## 6. HEALTH AND SAFETY

No significant health and safety issues are associated with the implementation of SEAR, other than the health and safety considerations normally associated with a remediation field demonstration.

## 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 injectant, 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, 2000; draft version). 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.

## 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 only treated 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

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Project No. 25

| Liquid Nitrogen Enhanced Remediation (LINER): A New Concept for the Stimulation of the Biological Degradation of Chlorinated Solvents |  |  |  |
| :---: | :---: | :---: | :---: |
| Location Netherlands | Project Status New project | Media Soil and groundwater | Technology Type |
| Technical Contact Arne Alphenaar, Emile Marnette, Haimo Tonnaer, | Project Dates | Contaminants VOCls |  |
| Chris Schuren, Frank Spuij, Andre Lokhorst (Tauw), Robert Nijhuis (AGA-gas) | Costs Documented? | Project Size | Results Available? |

## 1. INTRODUCTION

One of the major problems involved in soil remediation today is the treatment of deep groundwater contaminated with chlorinated hydrocarbons (VOCls). Biological degradation through microorganisms often will 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 infiltration systems tend to clog easily and the limited radius of influence of an infiltration well requires a dense network of wells.

In cooperation with AGA gas, engineering consultancy Tauw has developed a new remediation concept, which overcomes most of the limitations inherent to the conventional in situ biological systems for degradation of VOCls.

## 2. REMEDIATION OF SOIL CONTAMINATED WITH VOCLS

The Netherlands count large numbers of sites contaminated with VOCls. The remediation approach commonly applied concerns extraction of contaminated groundwater followed by above ground treatment. However, authorities more frequently impose severe restrictions on groundwater extraction. Insitu 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 contamination located in relatively shallow soil layers.

Over the past few years, a few methods have been developed to enhance indigenous biological degradation of ntaminants situated at greater depths; the local bacteria are stimulated such that they clean up the VOCls contamination. All these methods involve the infiltration of a substrate (to feed the bacteria) into the soil.


Figure 11: Schematic of the drawbacks of liquid substrate addition

## Problem: substrate transportation in the groundwater

All methods are based on adding and mixing substrate to the soil. Infiltrated substrate flowing along with groundwater will be degraded by all kinds of soil bacteria before it reaches other contaminated areas downstream. In consequence, the network of infiltration points required to effectively stimulate the existing natural attenuation processes will have to be very dense. The cost of such networks makes them practically unfeasible, particularly for contaminants located at large depths. Again, another problem involved in infiltration of substrates in liquid form is clogging of the wells by biomass.

## Solution: Gas injection substrate by means of infiltration.

The flow rate at which gas is distributed both horizontally and vertically within the soil is much higher than that of water, making the injection of gas a much more effective procedure. Another advantage lies in the relatively low cost of injecting gas into great depths.

Due to the (anaerobic) nature of microbiological processes, the use of compressed air is impossible. On the basis of recently obtained insights into the behaviour of indigenous microorganisms, the injection of nitrogen gas saturated with methanol (substrate) or of nitrogen-hydrogen mixture is currently under consideration.


Figure 12: Schematic view of the advantages of anaerobic sparging (the liner gas injection system)

A favourable side-effect of the method is that due to the stirring created in the soil by the injected gas (input of energy), contaminants will become more readily available for biological degradation or physical removal.

## LINER - Liquid Nitrogen Enhanced Remediation

LINER involves the injection of nitrogen gas saturated with a substrate. In April 2000, a pilot investigation began to test the feasibility and efficiency of LINER. It is expected that the project will serve to demonstrate in practice that gas injection is a feasible alternative to the in-situ remediation methods commonly applied to VOCls contamination. The following aspects of gas injection are investigated:

- Substrate injection procedures; particularly the injection of methanol as a substrate, in the form of a fine mist, has not reached the final development stages yet;
- Radius of influence and distribution pattern of the injected gas; and


Figure 13: Set-up of the Pilot Tests

The pilot will be integrated into a full-scale remedial operation. At two other sites, LINER will be applied at full scale as a remediation technique for VOCls. This approach offers a unique opportunity. The new technique can simultaneously be tested on a practice scale on three sites, with each site differing from the other ones in terms of soil structure, contamination situation, and remediation target.


LINER pilot setup

The picture shows the LINER pilot setup. Liquid nitrogen is evaporated. The built up pressure is reduced to the appropriate injection pressure. Via nozzles, methanol is nebulized into the nitrogen gas-flow.

The injection well is situated ${ }^{* *}$ m below grade. At several distances monitoring wells are installed for monitoring the distribution of methanol in the groundwater and for assessing the enhancement of biological degradation of VOCls.

## 3. PRELIMINARY RESULTS

The methanol has been retrieved in high concentrations-over $500 \mathrm{mg} / \mathrm{L}$ at a depth of 5 m below grade and approximately 200 $\mathrm{mg} / \mathrm{l}$ at 45 m below grade (the depth of injection). There has been a considerable distribution of methanol in a vertical direction. This observation indicates that the methanol vapor is stable enough to be distributed by the nitrogen gas flow.

Up until now, no methanol has been retrieved in monitoring wells that are located at lateral distances from the injection well. However, a large increase has been observed in degradation products of PCE and sulphate reduction.

| SIREN: Site for Innovative Research on Monitored Natural Attenuation |
| :--- | :--- | :--- | :--- |

## 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 that 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 characterised, will be open to any bona fide researcher to conduct research on natural attenuation funded by other bodies. AEA Technology, Shell, and the Environment Agency developed the project. In phase 1 of the programme, the project team formulated criteria for research site selection. These criteria were developed to locate a site available for 3-5 years that contained a mixture of contaminants in an aquifer characteristic of UK conditions. Herein, we present the results of the site selection process.

## 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.

## 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

In phase 1 of the project, the objective has been to identify a suitable demonstration site for monitoring natural attenuation. As part of this analysis, criteria were identified to assess the suitability of a number of sites. It was considered that the ideal site should:

- Contain potentially biodegradable contaminants in a groundwater plume and should not contain large amounts of free product.
- $\quad$ Be available for research for at least 3 years, although preferably 5 years.
- Have a plume of contamination that will not impact a receptor within 3 years of the project. The plume should be contained within the site boundary or access should be available to areas of the plume off-site.
- Have no current or impending legal and/or regulatory disputes.
- Have a limited number of identified source areas.
- Have sufficient initial site characterisation information to identify sources, pathways, and receptors.
- Have historical monitoring data that could act as a benchmark.
- Be situated on a minor sedimentary aquifer, with preference given to a consolidated formation, such as sandstone.
- Have groundwater within 10 to 15 m of the surface, and the water table should not be subject to wide fluctuations with recharge.
- Have no operating remediation scheme that could interfere with the potential study area.
- Be secure with no outstanding HS \& E issues.


## 5. RESULTS

Over 200 sites were considered. Of these, more than 60 were petrol and oil depots, 117 were infrastructure sites and more than 10 were landfills. Only 41 sites of this initial list were situated on a minor sedimentary aquifer. After taking into account site availability, that the contaminants need to be amenable to MNA, and that active remediation was not already underway or pending, just 4 sites were left for further ranking against the criteria in section 4.

The short-listed sites were 1) a landfill in the south of England; 2) a waste transfer station; 3) a petroleum distribution plant; and 4) a chemical plant. Although the landfill had received large amounts of liquid solvent waste (mainly toluene), the contamination plume was either already attenuated or ill defined. Moreover the presence of a deep unsaturated zone increased potential investigation costs. Consequently, the landfill was considered a low priority. The waste transfer station was leased to a chemical company and was located on 9 m of blown sand overlying Upper Carboniferous sandstone. Contaminants included PAHs, chlorinated hydrocarbons, and CFCs. However, further investigation indicated that the contaminants had migrated off-site with access to that part of the plume unlikely. In addition, the CFCs were regarded as non-biodegradable and, as such, this site was also designated "low priority." The petroleum distribution site was located on a consolidated aquifer, with plume flow towards a nearby river. It was a multi-occupant site with contamination that included fuel oils, petroleum hydrocarbons, and diesel. There were a limited number of source areas that had mainly been cleared. MNA had not been investigated in detail at this site, but in general the site did agree with the selection criteria. However, due to legal issues that could potentially arise from multi-ownership of the site, it was not ranked the highest of the short-listed sites.

The highest ranking was given to the chemical plant site with mixed contaminants including BTEX, chlorinated solvents, LNAPL, and DNAPL. It has both perched aquifers and a major consolidated aquifer that are contaminated and a number of receptors identified nearby. There is no evidence to date that these receptors have been impacted by contamination. The plume is not believed to have migrated off-site. The site has just one owner. The project team agreed that the contamination could be managed successfully by monitored natural attenuation (MNA). The chemical plant was, therefore, found to be the most compliant
with all of the site selection criteria. Moreover, a nested monitoring well network was already in place and being extended. As such, this site was chosen as the preferred location for the SIREN project.

## 6. HEALTH AND SAFETY

All projects proposed for the site will undergo a formal health and safety review. All staff involved with projects at the chosen SIREN site will undergo an initial site health and safety induction course.

## 7. ENVIRONMENTAL IMPACTS

Environmental impacts at the site will be marginal. Utilisation of MNA at this site will be a low energy/low impact approach.

## 8. COSTS

The Environment Agency is expected to contribute in the region of $£ 250 \mathrm{k}$ to the project with $£ 25 \mathrm{k}$ provided for the phase 1 project. During this initial phase of work, more than $£ 1 \mathrm{M}$ worth of site investigation work has been reviewed. In phase 2 of the work, in kind contributions from the project team should total about $£ 350 \mathrm{k}$. Through phase 3 , the project team is looking to manage in the order of $£ 1 \mathrm{M}$ per year in research grants.

## 9. CONCLUSIONS

During this first phase of SIREN, 203 sites were considered as possible field locations. Of these sites, about $20 \%$ were identified as being on minor sedimentary preferably consolidated aquifers. This is not surprising considering the fact that many contaminated sites in the UK are located in coastal regions or in valley deposits. The remaining stringent selection criteria eliminated the majority of these 41 sites, with the result that only 4 were considered to be serious candidates. Of these, a petroleum storage plant and a chemical plant were considered to be the most appropriate sites with the ownership issues weighing the final selection in favour of the chemical plant.

The site owners have since granted permission for phase 2 of the SIREN project to go ahead, and in principle have agreed for the site to be used as a demonstration site for 3-5 years subject to certain conditions of confidentiality and safety. A further advantage of this site is that its operator is already conducting a considerable amount of additional site characterisation and monitoring that will be made available to project SIREN. Taken as a whole, the contamination at the site is too complex to fit comfortably within SIREN without further site characterisation to enable clear objectives to be set for this project. This work will be carried out in phase 2 .

## 10. REFERENCES

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| Project No. 27 |  |  |  |
| :---: | :---: | :---: | :---: |
| Hydro-biological Controls on Transport and Remediation of Organic Pollutants for Contaminated Land |  |  |  |
| Location <br> Former gas works site, United Kingdom | Project Status <br> New project | Contaminants PAHs, phenols, substituted benzenes | Technology Type In situ bioremediation |
| Technical Contact <br> Prof. Howard Wheater <br>  | Project Dates <br> February 1998 - <br> February 2001 | Media <br> Soil and groundwater |  |
| Environmental Engineering, Imperial College of Science, Technology \& Medicine, London, SW7 2BU | Costs Documented? Yes | Project Size <br> Not available | Results Available? No |

## 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:

1. To 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. To assess in situ biodegradative activity in the vadose/unsaturated zone and evaluate potential for enhanced bioremediation.
3. To 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. To 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 3 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 $\mathrm{O}_{2} / \mathrm{CO}_{2}$ 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 ${ }^{14} \mathrm{C}$-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 airsparging, 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 <br> Soil and made ground |  |
| Tony Wakefield | August 2000 - |  |  |
| Wakefield House | September 2000 |  |  |
| Little Casterton Road |  |  |  |
| Stamford | Costs Documented? | Project Size | Results Available? |
| Lincolnshire | Yes | Demonstration | No |
| PE9 1BE |  |  |  |

## 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 $20 \mathrm{MW} / \mathrm{m}^{3}$. 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 | Monitoring |
| Technical Contact | Project Dates: | Media: |  |
| Dr. Claudio Mariotti | Start: |  |  |
| Dr. Leonardo Zan January 1998 <br> Aquater  |  |  |  |
|  |  |  |  |  |  |
| Via Mirabello 53 | End: <br> December 2000 |  |  |
| 61047 S. Lorenzo in Campo Italy |  |  |  |
|  |  |  |  |
| Tel: +39 07217311 | Costs Documented? | Project Size: | Results Available? |
| E-mail: <br> claudio mariott@ aquater eni it | Not yet | Test site | Not yet |

## 1. INTRODUCTION

This project is focused on an automatic remote controlled monitoring system of parameters and polluting processes for remediation of sites contaminated with petroleum products and byproducts. This project summary outlines the general procedure for project development.

The above-mentioned remediation works are both in situ or on site, based on integrated chemical-physical or microbiological processes, such as bioventing, air sparging and natural attenuation for in situ technologies, or biopile for on site technologies.

The main objectives of this monitoring and control system are:

- To assess environmental impact and ongoing polluting processes;
- To verify the level of contaminant removal achieved in the contaminated environmental components;
- To optimize the acquisition methods for physical, chemical and biological data;
- To substitute the manual sampling activities and laboratory analysis.

Development of this system is achieved through the following steps:

- Definition of process and environmental parameters to be monitored;
- Selection of suitable measuring gauges and analysis apparatus;
- Design of system architecture;
- System implementation; and
- Testing of system.


## 2. BACKGROUND

The project is a logical follow-up of a preliminary monitoring network developed under RESCOPP project. Project RESCOPP (REmediation of Soil COntaminated by Petroleum Products) (Project number Eu-813) was a cooperation between Italian and French companies carried out under EU EUREKA Funding Program during the period of 1993-1997.

The objective of the project was to develop innovative tools for monitoring and remediation of sites polluted by petroleum products.

## 3. TECHNICAL CONCEPT

## Controlled process parameters

To achieve effective remediation that interacts with the three environmental components in the subsoil (interstitial gas, soil, and groundwater), the minimum set of parameters to be controlled in order to assess both the evolution of ongoing processes and the system's quality are:

## Interstitial gas:

- VOCs;
- $\quad \mathrm{CO}_{2}$;
- $\mathrm{O}_{2}$;
- $\mathrm{CH}_{4}$; and
- pressure;


## Soil in the vadose zone:

- temperature; and
- humidity;

Groundwater:

- level;
- temperature;
- $\quad \mathrm{pH}$, Eh, electrical conductivity; dissolved $\mathrm{O}_{2}$;
- TPH;
- BTEX; and
- total heterotrophs.

It is also necessary to monitor the meteorological parameters that affect both data quality and the evolution of all processes involved during remediation. These parameters are:

## Meteorological parameters:

- temperature;
- barometric pressure;
- humidity;
- solar radiation;
- wind speed and direction; and
- rainfall.


## 4. ANALYTICAL APPROACH

## Measuring principles

The analysis apparatus and measuring gauges that compose the monitoring system must meet the following requirements:

- The quality of analytical data must be comparable to those obtained in the laboratory in regard to precision and accuracy of measurements.


## System architecture

The elements that compose the automatic system are:

- Monitoring and sampling points;
- Measuring gauges;
- Analytical equipment for gas and water samples;
- Gas and water sampling apparatus;
- Interface for measuring signals with data acquisition units;
- Local data acquisition and system management unit;
- Management software;
- Data transmission;
- Remote data acquisition and control unit;
- Monitoring of chemical-physical variations induced by the system; and
- Final control of remedial system.


## 5. RESULTS

Results of the onsite test on a biopile will be available in December 2000.

## 6. HEALTH AND SAFETY

The system is totally health safe; in fact it avoids any direct contact with toxic chemicals.

## 7. ENVIRONMENTAL IMPACTS

The goal of the project is to monitor the progress of remediation techniques in a polluted site and contaminant environmental evolution by an early and remote warning system. The system itself does not imply any particular environmental impact.

## 8. COSTS

The total project cost is estimated in about 300,000 US $\$$.

## 9. CONCLUSIONS

Work is still in progress.

## 10. REFERENCES

RESCOPP project report (Eureka Eu-813)

## ARMENIA

## 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 reprocessed 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 $\% 1 \mathrm{~m}^{2}$ | $1-5$ |
| 9. | Content of useful metals $\% 1 \mathrm{~m}^{2}$ | $1-5$ |
| 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 and every 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 neolandscapes 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 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 $10-15 \mathrm{~cm}$-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 $10-15 \mathrm{~cm}$-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 | $\begin{gathered} \hline \text { Volume } \\ \mathrm{M} \mathrm{~m}^{3} \end{gathered}$ | Particles average diameter | Waste content |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1. | Right-bank tributary to Vokhchi River, Village of Darazam | 1953 | 1961 | 3 | 0.067 | $\begin{gathered} \mathrm{Mo} \\ \mathrm{Cu} \\ \mathrm{SiO}_{2} \end{gathered}$ |
| 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 | $\mathrm{Al}_{2} \mathrm{O}_{3}$ |
| 7. | In gorge No. 1 of Agarak | 1978 | Working | 9 | -"- | $\begin{gathered} \mathrm{MgO} \\ \mathrm{CaO} \end{gathered}$ |
| 8. | In gorge No. 2 of Agarak | 1979 | Working | 17 | -"- | $\begin{aligned} & \mathrm{TiO}_{2} \\ & \mathrm{FeO} \end{aligned}$ |
| 9. | In gorge No. 3 of Agarak |  |  |  |  | $\begin{gathered} \mathrm{Na}_{2}+\mathrm{K}_{2} \\ \mathrm{O} \\ \mathrm{P}_{2} \mathrm{O}_{5} \end{gathered}$ |
| 10. | On Nahatak River nearby settlement of Akhtala | 1971 | 1988 | 3.2 | 0.082 | $\begin{gathered} \mathrm{S} \\ \mathrm{Zn} \\ \mathrm{~Pb} \end{gathered}$ |
| 11. | Nearby Village of Arazap (Province of Ararat) | 1982 | Working | 20 | 0.085 | rare metals |
| 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 $\qquad$ Characteristics (point) |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 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 |


#### Abstract

AUSTRIA

\section*{1. LEGAL AND ADMINISTRATIVE ISSUES}

Austria has a Federal Act on the Clean-up of Contaminated Sites (ALSAG) since 1989. The main focus of this act is to provide a state-fund for remediation via a waste tax. The amount of waste tax depends on the technical standard of the landfill to which waste is brought to today. 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 Ministry for Agriculture, Forestry, Environment and Water Management is working on an amendment to 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. Also the polluter-pays-principle should be strengthened in the amendment.

The EU DG Competion wants to launch a guideline restricting state funding for remediation projects for companies even more. For Austria this will cause a significant slow-down of remediation of contaminated sites because all remediation activities up to now are based on state funding. So Austria supports the statement of Clarinet to rethink this guideline and to exclude remediation funding from that guideline.

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 Ministry for Agriculture, Forestry, Environment and Water Management registered by January 2000 2.499 suspected sites of which 2.316 are landfills and 183 are industrial sites. Detailed risk assessments showed that 148 sites pose a considerable risk to human health or the environment and therefore were classified as contaminated sites.

For the time being 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 Ministry for Agriculture, Forestry, Environment and Water Management. In the last ten years 97 remediation projects, with a total cost of ATS 3,4 billion (approx. 283 US\$) were funded.

## 3. TECHNOLOGY DEVELOPMENT PROGRAM

There is no specific technology development program on a federal level. Initiatives are set by defining a list of priorities for funding research via the Kommunalkredit Austria AG.

## 4. REMEDIAL METHODS IN USE

| "Safeguarding" Methods: |  |
| :--- | :--- |
| capping of landfill |  |
| extraction of landfill gas |  |
| enclosure | 31 |
| hydraulic measures | 32 |
| pump and treat | 38 |
| in-situ sorting of material | 20 |
|  | 9 |


| Remediation Methods: | Number: |
| :--- | :---: |
|  | 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

"Contaminated Sites - Risk Assessment concerning the Pollution of Soil-Air," Austrian Standards Institute
"Application of Bioassays for Risk Assessment and Risk Monitoring of PAH-contaminated Sites," IFATulln
"Investigation and Assessment of Potential Waste Sites in Styria (Austria)," Joanneum Research, Graz "Evaluation and Preliminary Assessment of Old Deposits," Landesakademie Lower Austria
"Mechanico-biological Treatment of Mass Waste," University Leoben
"Comparison of Elution Tests on Solidified Waste," University for Agriculture, Vienna
"Material-technological Examinations on Solidified Waste," University Innsbruck
"Evaluation of Testing Methods and Models for Valuing the Medium and Long-term Emissions of an Organic Waste," University for Agriculture, Vienna
"New Models for Waste Tax," Quantum, Klagenfurt
"Examination of Heavy Metals in Thermal Treatment Residues," University for Agriculture, Vienna
"Guideline for Treatment of Electronic Waste," Technisches Büro für Technischen Umweltschutz, Vienna
"Treatment of old Wood, especially from Furniture," TechSET, Vienna
"Treatment of Laqueur Waste," AFC Aforma Consult GmbH, Vienna
"Treatment of Galvanic Sludge," AFC Aforma Consult GmbH, Vienna
"Treatment of used Batteries," OekoConsult GmbH, Vienna
"Realisation of the Concept of Treating Medical waste," IC Consulenten ZT GmbH/KMB, Vienna
"Technologies for cleaning Air from mechanico-biological Treatment," Institute for Industriell Ecology, St. Pölten
"Mechanical Treatment of Electronic Waste," University for Agriculture, Vienna
"Treatment of old Oil and Fat," AFC Aforma Consult GmbH, Vienna

## 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 few 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.

## B. Summary of Legislation

Until now, only Flanders has adopted a full legislative framework. 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 (see Annual Reports 1996 and 1998). They cover five key-issues:

- a register of polluted sites;
- the distinction between historical and new soil contamination;
- the distinction between duty and liability for remediation;
- the soil remediation compulsory procedure and control;
- the transfer of land.

Soil standards, background levels, and intervention values have been adopted by the Flemish Government. The intervention values 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.

The two others Regions, Brussels and Wallonia, have partial legislations, based mainly on Waste Decrees and on Town and Country Planning provisions. Since 1999, both Regions 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 uses authorized in the surrounding area. Those new 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 was adopted, in April 2000, 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, in May 2000, the Walloon Government has launched a Strategic Programme for Contaminated Soils and Brownfield Sites, including the preparation of a comprehensive Soil Decree. This programme should be implemented and presented to the Walloon Parliament for adoption within the next 24 months, after hearings involving all public and private stakeholders.

During this period, transitory measures will enhance the rhythm of brownfield sites reclamation; they will also 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:

- OVAM (Public Waste Agency of Flanders) is the responsible authority for soil control and remediation in the Flemish Region.
- In Brussels 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. 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
- and whenever the license has to be renewed.

All information on soil pollution is compiled in the soil register, which serves as a database 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 remediation, in order to avoid to be listed as contaminated in the register.

For more details, see previous NATO/CCMS Annual Reports.

## Wallonia:

A registration system has existed since 1978 for derelict land and brownfield sites, based on Town and Country Planning legislation and aiming at the redevelopment of those sites (see previous reports). The transitory measures (see § 1.b) will not only update this registration system, but also 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 a list of sites for which a remediation plan should be prepared, has been approved, or is into execution (+/- 850 sites registered in 1999).

## Brussels Region:

No registration system is known at this moment. A first investigations/mapping strategy is in preparation.

## 3. REMEDIAL METHODS IN USE

Until recently, there have been no comprehensive statistics on remedial methods and technologies used for cleanup 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 and biological remediation techniques, electro-reclamation, infiltration and wash out.
*Data collected with the help of Ecorem n.v.


## 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 microorganisms in a slurry-reactor.
3. Phytoextraction 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.

In Flanders, a risk-evaluation model was evaluated and approved by OVAM. Research has been implemented on the prioritization of historical soil pollution, and a decision-supporting system has been developed to estimate which technologies are most appropriate at this moment, taking the costs into account.

VITO (The Flemish Applied Research Institute) is currently engaged in the following R\&D activities:

- inorganic reactive barriers (zero valent iron): treatability studies, material selection, circumventing clogging, protocol development for deployment and monitoring;
- biological permeable reactive barriers and permeable barriers for mixed pollution;
- circumventing bio-availability limitations for bioremediation of PAH and mineral oil;
- developing protocols for monitoring of natural attenuation, in-situ bioremediation and pump \& treat remediation as well as field monitoring for these technologies;
- phytoremediation;
- bioremediation of TNT.


## 5. CONCLUSIONS

Since the adoption of the Flemish Decree on soil remediation, there has been a growing recognition of soil and groundwater contamination issues in Belgium. Forthcoming months might see new developments, this time in Wallonia.

In the Flemish Region, the Decree has a highly positive influence on soil management and soil environmental quality.

However, the main problems will probably remain in the three Regions:

- the lack of resources of many liable parties, for the cleanup of historical pollution;
- the cost-efficiency and environmental merit of the remediation programs, whether funded by public or private money; and
- how will it be possible to reconcile 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

## 1. LEGAL AND ADMINISTRATIVE ISSUES

Canada is a country of 9,970,610 square kilometers and a population of 30 million inhabitants. The country's political structure is federalist, divided in 10 provinces and 3 territories with the recent creation, in 1999, of Nunavut Territory. The Canadian constitution leaves authority of non-federal contaminated sites with the provinces and territories for which they exist. Most provinces have established their own regulations or guidelines. Federal lands, which represent about $41 \%$ of the Canadian lands, are not subject to provincial/territorial legislation.

There are three federal Acts that are applicable to all Canadian lands:
The Canadian Environmental Protection Act, which states that if a person releases a regulated toxic substance into the environment, this person must take all reasonable emergency measures to remedy any dangerous condition or reduce/mitigate any danger resulting from the release. There are a number of regulations under the CEPA that may affect the management of contaminated sites. These include the Polychlorinated Biphenyls (PCB) Regulations, the PCB Treatment and Destruction Regulations, Storage of PCB Material Regulations and Contaminated Fuel Regulations;

The Fisheries Act, which stipulates that no work or undertaking shall be carried out that may result in harmful alteration, disruption or destruction of fish habitat, unless authorized by the Minister or by regulation. Further, it is an offence to deposit or allow the deposit of any deleterious substances in waters frequented by fish, unless authorized by regulation under the Fisheries Act or another Federal Act. The Act also specifies that if anyone is to engage in any work which may result in the disruption or destruction of fish habitat, or to deposit a deleterious substance in water frequented by fish, then plans, studies and specifications of the procedure must be provided to the Minister and;

The Canadian Environmental Assessment Act (CEAA) which requires an Environmental Assessment (EA) if an activity falls within the definition of "project" on CEAA's Inclusion List. As of June 1999, the remediation of contaminated sites has been added to this List and therefore requires an EA.

## 2. REGISTRATION OF CONTAMINATED SITES

The nature and number of contaminated sites, which exist in Canada, are not fully known, however, most provinces hold some type of registry of the environmental condition of lands containing general information on contaminated sites. These data banks are used primarily for statistical and report production purposes and are updated regularly. In most cases, sites have already been investigated and require minor remediation, or have already been cleaned up to government requirements.

In terms of federally owned sites, the Office of the Auditor General of Canada has estimated that there are 5000 federal contaminated sites, with an associated cleanup cost of $\$ 2$ billion, although these numbers have not been confirmed.

The Treasury Board Secretariat of Canada has recently released a Contaminated Sites Inventory Policy. The Policy's objective is to provide Canadian Parliament, the public, and federal departmental managers with complete, accurate and consistent information on federal contaminated sites and solid waste landfills.

By April 2001, all federal departments are required to establish and maintain a database of their contaminated sites and solid waste landfills. This information will then be incorporated into a central Federal Contaminated Sites and Landfills Inventory.

In addition to the inventory policy, a second Policy on Accounting for Costs and Liabilities Related to Contaminated Sites was released in 2000 by the Treasury Board Secretariat. In the interest of improved
financial reporting and to comply with the evolving requirements of the accounting profession, the intent is to capture and record federal liabilities for the remediation of contaminated sites. Significant environmental liabilities exist and will impact both the fiscal framework and the accumulated deficit of the government. In order to provide a fair and comprehensive statement of the government's financial position, it is necessary to identify, quantify and record these liabilities.

In 1989, the Canadian Council of Ministers of the Environment initiated the five-year, $\$ 250$ million (50\% federal) National Contaminated Sites Remediation Program. The program remediated 45 orphan sitessites for which the owner cannot be found, or is unable to pay for remediation-demonstrated over 50 technologies, and assessed 325 and remediated 18 federal sites. Scientific tools such as soil quality guidelines and the National Classification System, which ranks sites based on health and environmental risks, were also developed.

These tools are still used by many federal departments and by provincial and municipal governments. Since the program ended in 1995, significant progress on the assessment and remediation of federal contaminated sites has been made by federal government departments. Current spending on this issue averages about Can $\$ 94$ million per year.

## Sydney Tar Ponds

In 1998, the federal government approved Can\$41.5M over 3 years to address the Muggah Creek Watershed in Nova Scotia, which rests within an urban area setting and is home to the worst hazardous waste site in Canada. The watershed is 22.44 square kilometers ( 22,400 hectares) and encompasses the Tar Ponds, the former Coke Ovens site and the Municipal Landfill site. The contamination includes polycyclic aromatic hydrocarbons (PAHs), heterocyclic compounds, PCBs and heavy metals.

Selection of appropriate remediation technologies to remediation this site will involve bench and fieldscale evaluations. This technology demonstration program is currently underway at an estimated cost of Can\$ 5 million.

## 3. REMEDIAL METHODS IN USE

Canadian contaminated sites are generally categorized as follows:

- Unregulated former 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 1997, a general reference manual entitled: "Site Remediation Technologies" was published for federal employees involved with site remediation work.

The following is a summary of the reference manual reflecting Canadian general remediation strategies and related technologies.

In-situ Remediation of Soil and Groundwater

- Soil Vacuum Extraction
- Bioremediation (bioventing, bioslurping, land treatment)
- Soil Flushing
- Thermal Treatment (volatilization, solidification)
- Electrokinetics
- Phytoremediation
- Treatment Walls

Pump and Treatment of Groundwater

- Air Stripping
- Steam Stripping
- Advanced Oxidation
- Carbon Adsorption
- Bioreactors
- Membrane Separation
- Oxidation/reduction
- Ion Exchange
- Precipitation
- Coagulation/Flocculation
- Filtration

In-situ Containment

- Slurry Walls
- Grout Curtains
- Sheet Pile Walls
- $\quad$ Surface Caps

Ex-situ Remediation of Excavated Materials

- Soil Washing
- Thermal
- Biological
- Chemical
- Metal Extraction
- Fixation/Stabilization
- Disposal (industrial/municipal landfills, hazardous waste disposal, aquatic disposal, storage, reuse/recycle)


## 4. RESEARCH AND DEVELOPMENT ACTIVITIES

Several universities and research institutes across country dedicate their work to groundwater contamination, soil remediation technologies, sediments contamination and biotechnology.

Although federal funds are not currently committed specifically to contaminated sites technology development, there are numerous federal initiatives which provide indirect funding for advancement and promotion of remediation technology such as: Sydney Tar Ponds Clean-up, Technology Partnerships Canada, Industry Canada's Environmental Solutions Database, etc.

## 5. CONCLUSIONS

Contaminated sites remain an issue of concern for Canadian governments and private industry. Despite the absence of a national approach, federal, provincial, and territorial governments have made significant progress on the assessment and remediation of their contaminated sites. Advancement in contaminated site technologies and site cleanups will continue to be addressed as an important environmental challenge.

## CZECH REPUBLIC

In previous years we've informed you about remediation experience in the Czech Republic with emphasis on remediation works in localities, which left the Soviet Army. Allow me please today, to introduce you to more experience gained in the Czech Republic in the field of the environment, namely, in the process of large-scale privatisation because I receive more and more questions on this topic.

The rehabilitation of environmental burdens requires large financial resources; therefore, in the Czech Republic the principle of finding a socially acceptable (reasonable) level of environmental as well as health hazards has been applied also bearing in mind that attaining of "zero risk" is not always necessary from the environmental point of view and often is accompanied with unreasonably high costs incurred.

In context of the Czech Republic joining to the member states of the European Union, certainly a major emphasis is put on remedial of contaminated sites also, among other things, for the reason that this is the condition of foreign investors' interest in investments into Czech companies.

There is no specific act providing for remedial of environmental burdens in general in the Czech Republic. The legislation, which is especially important for environmental burdens in rocks and in groundwater, comprises of the Act No. 92/1991 Code, on conditions and terms of the transfer of government property onto other entities, Act No. 171/1991 Code, about Fund of National Property (FNP) of the Czech Republic and also the Act no. 138/1973 Code, on water as amended by the Act No. 14/1998 Code, and the Act No. 125/1997 Code, on waste.

Remedial measures done by privatised companies are reimbursed by the FNP from finances gained in the privatisation process, which do not belong to the state budget.

The principle documents governing remedial of contaminated sites in the privatisation process are the Decisions of the Government of CR No. 123/1993 and No. 810/1997. These documents establish that every obligation to environmental burdens (contaminated sites) are transferred onto the proprietor to be of the property privatised. Government, however, as the former proprietor is responsible for remedial of contaminated sites, which contamination occurred before they were privatised. The decisions include concrete lists establishing environmental damages (as groundwater contamination, soil contamination, existence of hazardous waste landfills on the company sites, and contaminated structures and sites or portions thereof). These two decisions further establish the procedure, which these damages to the property may be solved.

The first step that the proprietor of the privatised property shall make on the basis of the Act No. 92/1991 Code is to elaborate eco-audit of the property privatised. Then, based on the consent of the Government of the Czech Republic, the Fund of National Property shall conclude an agreement with the transferee (so called environmental agreement) in which the Government undertakes the reimbursement of costs made in remedial actions of contaminated sites. Maximum of the costs is limited to the amount of purchase price of the property privatised, or to equity capital of the company in case of joint-stock companies.

The next step is making a risk analysis. This works are covered by the Fund of National Property from the account budgeted for rehabilitation of contaminated sites and the supplier thereof is selected in a tender. On the basis of the risk analysis results, the administrative body of the Ministry of the Environment of the Czech Republic, which is the Czech Environmental Inspection (CEI) here, shall make a decision on remedial measures establishing concrete extent of the environmental burden and concrete levels (values) and deadlines that shall become the targets of the future on-site remedial action. A separate tender is called for the supplier of the remedial action.

From 1991 to March 15, 2000 the number of the environmental agreements approved by the Government and concluded by the Fund of National Property reached 234 resulting in guaranteed amount about CZK 136 billion, while it is assumed that actually drawn amount to be CZK 32 billion. By December 31, 1999

FNP spent approximately CZK 7.2 billion for cleanup of contaminated sites, out of the amount about CZK 1.8 billion (approximately 200 million USD) in 1999. FNP has registered approximately 220 actions, in which cleanup of old contaminated sites has been implemented. Five cleanups were finished and $60 \%$ of the rest are in the preparatory phase (tenders for risk analysis elaboration or the administrative procedures for issuing of the CEI decision have started). In case of the remaining $40 \%$ of the actions, remedial works are carried out or post cleanup monitoring is performed under control of supervisors who control usefulness of the finances spent.

The estimate of future guarantees for contaminated sites, in cases of further privatisation and condition to that the Government approves further environmental agreements, is at the amount of roughly CZK 165 billion, while it is assumed that actually drawn amount to be CZK 46 billion.

Last year, however, the solving process of environmental obligations in privatisation was sluggish due to FNP, yet in the end a series of hard negotiations resulted in the Government Decision No. 917, adopted on September 8, 1999, and ordering the continuation in reimbursing of environmental obligations based on already signed environmental agreements and also in concluding of new environmental agreements in accordance with the effective rules.

As of yet substantial contaminated sites, for example, in companies privatised in the first wave of the privatisation when the duty to elaborate the eco-audit was not established yet have not been solved. The manner of cleanup actions on lands not belonging to the entities, who are bound to perform remedial measures, and in case of proprietors of restituted property has not been fully set. The government participation has not been completely defined even in case of companies in process of dissolution, which finances do not cover the necessary cleanup, and in case of residual companies as well. Concerning these cases for some of them the legislation that became effective at the beginning of 1998 is important. The importance is based on section 27 of the Act No. 14/1998 Code, modifying and amending the Act No. 138/1973 Code, on water, which establishes the state of facts, in which costs related to the remedial measures are reimbursed by appropriate district government in cases as listed in the Act if there is a risk of delay (for example, the incomplete or not performed remedial action may pose a risk to a water source).

At present a bill amending the water act defining the area more exactly especially in determining the duty of district governments to allocate the annual reserve at the amount of CZK 50 million for the actions that are inevitable to be performed in the area, is ready for negotiations.

The contaminated sites are assessed form the point of view if they pose substantial risk to the environment and human yet so far they have not been prioritised in accordance with officially established priorities. It follows from the fact that decisions on privatisation were also made step by step and so there was impossible to wait till decisions on all companies, which had substantially contaminated sites, are made. A list of all contaminated sites (irrespectively there are finances for funding appropriate remedial measures at present) that are necessary to be cleaned-up with high priority has been worked out at the Ministry of the Environment in co-operation with CEI and Territorial Departments of the ME. Respective lists of every region were completed and work on list of whole the CR will continue. The Ministry set up additional criteria for objective assessment of seriousness of contamination based on a rather broad context. Basic criterion is the potential of putting at risk resources of mass supplies of drinking water.

Mention should also be made of the database that originated at ME in connection with projects to support the environment. This is the SESEZ database (list of environmental burdens from the past), which constitutes a step of ME towards gradual filing of information on all environmental burdens. The database is filled with records of investigation and decontamination work at individual locations. There are several sources of data, consisting in the databases of gradually created records of cases resolved by the Department of Environmental Burdens and the National Property Fund, including records of decontamination of pollution caused by the stay of the Soviet Army. Another source in the future should consist in information from the District Authorities on decontamination or other work that is not paid for
by the state budget or from the funds of ME or NPF. This is an instrument intended for the District Authorities and state administration for keeping records of environmental burdens from the past. At the present time, the central database contains records of about 900 locations and the work has not yet been completed (contact: GRUNTORAD JAN@env.cz)

At present the discussion on whether remedial of contaminated sites is sufficiently effective goes on in the Czech Republic, as elsewhere in the world, and the entire system has been gradually improved by adding more and more check elements.

I believe that my contribution made you confirmed that we in the Czech Republic thoughtfully devoted our attention to the environment already at the beginning of establishing of privatisation rules.

It is a matter of fact that not all decisions on privatisation came right but, there is no doubt that it was the privatisation process, which started the entirely different approach in practical reality to the environment compared to that, which had been in the country before, and the privatisation has had clearly beneficial influence on the quality of the environment in our country.

Besides, the remedial of contaminated sites that left the Soviet Army has been financed through the state budget.

In the period from 1990 till the end of 1999 the amount allocated in the state budget for survey and cleanup works, including risk analysis and supervisory assessments reached approximately CZK 974 million. Today it is expected that by 2008 there shall be a need for further CZK $300-400$ million. We still work on 6 localities. Total costs just for works of cleanup of groundwater, soil, and uncontrolled dumpsites shall account for approximately CZK 1.3 to 1.4 billion. These finances shall cover the achievement of just acceptable, and that I must emphasize, level of environmental pollution and enable for reasonable use of such areas in the Czech Republic.

The sites with the most extensive contaminated areas and degree of risk include the former Hradčany airport in the Ralsko area and around Milovice (originally the Mladá Military Training Area). Extensive contamination of ground waters and soil by aircraft kerosene and chlorinated hydrocarbons has been found in the area of the Hradčany airfield. The usual chief centers of contamination mostly lie in the vicinity of the original locations of warehouses of automotive fuels and uncontrolled hazardous waste dumps. The seriousness of this contamination is increased at this site by the fact that the territory lies in a very important hydrogeological region (the territory is located in a protected area of natural accumulation of water from the North Bohemian Cretaceous and the amount of water in the geological basement has been estimated at several billion $\mathrm{m}^{3}$ ). The usable supplies of underground water equal 2380 1.s ${ }^{-1}$.

An area of approximately 15 ha is designated for remediation with the target of attaining a limit of 5000 $\mathrm{mg} . \mathrm{kg}^{-1}$ of dry matter of petroleum hydrocarbons (NES) in the soil and $5 \mathrm{mg} . \mathrm{l}^{-1} \mathrm{NES}$ in the ground water.

The maximum pollution is located in the vicinity of the ground water surface level, which is 4-6 m under the surface. The average concentration of NES in soils is $11000 \mathrm{mg} \cdot \mathrm{kg}^{-1}$ and a separate phase of these substances is also frequently present on the surface of the underground water. The decontamination of the ground water (collection of the phase of petroleum products, stripping), decontamination of the soil air (venting) and decontamination of soil in situ by air sparging is continuing. Autochtonnic microorganisms are used and nutrients (nitrogen, phosphorum) are added to increase the biodegradation activity; the effect of surfactants is also being tested. So far, approx. 1150 tons of petroleum hydrocarbons have been removed and a further minimally 1500 tons of contaminants will have to be removed to achieve the set limit. It is expected that decontamination of territory will be completed by the year 2008.

In the former Mladá MTA work is continuing primarily at the Milovice camp and Milovice airfield at Boží Dar. Contamination at these sites consists mainly of aircraft kerosene, gasoline, diesel fuel, oil, and paint thinners. This area is also of great importance for water supplies, from the Dolní Pojizeří area. These
are sources with an extensive collection system that are significant not only for their yields - a total of 1800 1.s ${ }^{-1}$, but also for their quality. They provide $20 \%$ of the overall requirements of Prague.

Decontamination of groundwater is progressing at both of these localities (collection of the separate phase of petroleum substances, stripping), along with decontamination of the soil and decontamination of soil air by venting. It is expected that the decontamination work will be completed at the Milovice airfield site in the year 2005 and at the Milovice campsite in the year 2007.

## RESEARCH AND DEVELOPMENT PROJECTS

In the year 2000, the Ministry of the Environment is providing support for specific research and development programs. Calls for tenders have been announced for work on the following programs related to the subject of elimination of environmental burdens from the past:

## Environmental Economics

- Draft strategy of financing environmental protection

The goal of the project is to prepare proposals for financial provision for decisive targets for the future, in accord with the new environmental policy, in particular to analyze current sources of financial protection of the environment-especially the State Environmental Fund, the state budget, the National Property Fund, sources at a local (regional) level, private sources, foreign sources, etc. In addition, it is required to specify the necessary financial sources for protection of the environment, primarily on the basis of completed quantification of expenditures connected with harmonization with the EU . It is necessary to elaborate the basic principles of financial policy for the area of protection of the environment.

Time period: 2000-2001
Number: VaV/320/5/00
Support: 2463000 CZK

## Environmental Burdens from the Past

The goal of the program consists in theoretical evaluation of the risk entailed in biodegradation of aromatic chlorinated hydrocarbons and preparation of basic principles for identification of natural biodegradation of important contaminants in the geological environment and decontamination technology for liquidation of the contamination. The target of the project also consists in study of the transformation of specified contaminants (PAH, phenols), the toxicological properties of the intermediates in their degradation, monitoring of their migration, the detection and decontamination limits, and determining the conditions, effects and specifications controlling transformations of specified contaminants and monitoring in practice at selected locations.

Time period: 2000-2001
Number: VaV/730/1/00
Support: 988000 CZK

Waste
The goal of the program consists in waste management and replacement of technical fuels, more intensive collection, transportation and separation of municipal waste, development of new composite materials made from recycled plastics for more competitive products, proposal of technology for processing of the biodegradable components of waste.

Time period: 2000-2003
Number: VaV/720/1/00
VaV/720/2/00
VaV/720/4/00
Support: 6182000 CZK

## FINLAND

I have a pleasure on behalf of the Ministry of Environment in Finland to present the tour de table about progress in Finland.

In Finland, problems related to contaminated soil have been tackled systematically since the late 1980s. The first policy statement on contaminated soil question was given in 1988 by the Council of State: According the objective of that statement "contaminated land will be studied and cleaned systematically. Urgent cases will be cleaned as the need is established. Studies will be made of contaminated areas and steps will be taken as necessary to clean them systematically."

According this statement there was also "necessary to arrange the environmental authorities, to investigate cleanup techniques, and to make revisions in legislation. In any case as far as possible the polluter pays principle will be held in to meeting costs," said the Council of State.

At the moment almost all that is done first survey and after that started remediation phase in 1995. Legal background has been refreshed in many steps. The last two most modern acts are:

1. New Act for Environmental Protection entered in force in 1.3.2000. This new piece of legislation includes soil protection, groundwater protection and also remediation procedure questions all together in one act.
2. New Building and Construction Act entered in force 1.1.2000. According that act, the construction site must be clean and land quality must be taken in account in physical planning and all land use.

Administrative structure is now simple and effective. Ministry is responsible on strategic and policy and also legislative issues, 13 regional authorities: environmental centres are responsible of allocation public funding, planning and decision making in permitting all - public and private remedial actions on contaminated sites. Finnish environmental institute conducts environmental R\&D. In generally the owner of real estate has environmental and economical responsibility of all old soil contamination. Secondary responsibility is shared between municipalities and state.

Ministry on Environment, the Association of Finnish Local Authorities and The Finnish Petroleum Federation have programme for the remediation of sites, which have been used for retail sale of petroleum products. Since 1996 has hundreds of those gasoline stations successful been cleaned up. Older, already closed cases are paid by The Finnish Oil Pollution Compensation Fund and those that will be closed are paid by oil companies.

In Finland are according the updated mapping about 20000 preliminary suspected case of which will be cleaned approximately $10 \%$. Current soil contamination will be cleaned in some ten years. Typically contaminated sites are in general civil sites instead of few military sites, land was not occupied under last great war, chemical industry is young, post war built, population is small and land great.

At the moment Finnish environmental centres are reporting quite broad survey and risk assessment project on soil pollution on shooting ranges caused by lead. Hundreds civil shotgun ranges are spreading lead broadly to surroundings, forest soil and groundwater. Rifle ranges, military or civil ones do not spread contamination to large area.

There are no derelict former industrial or military sites, so called brown fields, in Finland. All former important industrial sites near cities has until now-as well in future-been remediated and taken to other use, such as housing. The owners of the site are liable for the cleanup.

## FRANCE

In France, after one year, there are very limited changes in the field of polluted sites, and the situation described in the tour de table presented in Angers and included in the 1999 Annual Report remain valid. The only new element is the issue, on December 10, 1999, by the Ministry in charge of the Environment of a circular letter on "the principles of fixation of rehabilitation objectives."

According to this circular letter, the rehabilitation objectives are determined on the bases of a detailed evaluation study (in depth diagnosis) that describes and quantifies pollution source(s), pollution transfers, human and environmental receptors associated with a detailed (quantified) risk assessment considering human health and the environment (water, ecosystems). The application of the procedure takes in account the present and future use of the site and for human risk assessment the calculation of total exposure has to be compared to the tolerable daily intake for non-cancer effect substances and for carcinogens the maximum acceptable dose corresponds to a supplemental cancer risk of $10^{-5}$ for lifetime exposure.

A technical guide describing the methodology for this in depth diagnosis and detailed risk assessment will be published in the middle of this year.

## GERBER SITE IN SERMAISE

## A. Final Report On the Treatment of Polluted Soils by Solvent Extraction

During the previous NATO CCMS meeting in may 1999 in Angers a technical tour was organized to the Gerber site in Sermaise and the participants visited the on going treatment of polluted soils previously extracted.

The pollutants were mainly organics (BTX), chlorinated organics (solvents), PCB, heavy metals (lead, zinc) and the soil was specially difficult to treat because of heterogeneity, compacity, and high percentage of fine material. The treatment was realized by solvent extraction, named SOLVIS of the GEOCLEAN Company, using dichloromethane. Because of the risks associated with the extracting solvent a strict control of the operation has been continuously carried out (safety of workers and impact on the environment). The soil to be treated was classified in two categories stored separately: storage T of heavily polluted soil, lagoon $L$ of mean polluted soil.

The management of treated soil was realized as it follows:
As a general result, the total quantity of polluted soil has been treated according to the depollution goals for organics and chlorinated organics and is stored on the site.

Part of the treated soil did not reached the objectives for heavy metals (the treatment is not effective for inorganics) and was transported to be landfilled in a site authorized for the storage of special industrial waste.

Limited quantities of stones and waste (plastics and distillation residues) were separated before the treatment of polluted soil, stones being reused on the site after washing and waste being transported for treatment off site.

## B. Results

1. Total quantity of soil treated: 10650 tons

Treated soil remaining of the site: 9085 tons
Treated soil transported and landfilled: 1575 tons
2. Treatment of T storage

|  | Average pollution levels <br> before treatment (ppm) | Average pollution levels <br> after treatment (ppm) | Efficiency (\%) |
| :--- | :---: | :---: | :---: |
| PCB | 370 | 9.85 | 97 |
| BTX | 2400 | 19.2 | 99.2 |
| Chl SOLVENTS | 960 | 10.3 | 98.9 |

3. Treatment of $L$ storage

|  | Average pollution levels <br> before treatment (ppm) | Average pollution <br> levels after treatment <br> $(\mathrm{ppm})$ | Efficiency (\%) |
| :--- | :---: | :---: | :---: |
| PCB | 80 | 4.3 | 94.6 |
| BTX | 79 | 4.9 | 93.8 |
| Chl SOLVENTS | 360 | 6.4 | 98.2 |

C. Present Situation and Perspectives

The treatment of the polluted soils stored above ground was completed at the end of October 1999. Since then a new step has been initiated including:

- a first project of source reduction with the objective to extract and treat waste and heavily polluted soil still remaining under concrete covered area; and
- an additional study to complete the risk assessment realized in 1998 and to have a detailed description and quantification of the mechanisms of natural attenuation that appears to occur on this site.


## GERMANY

## 1. LEGAL AND ADMINISTRATIVE ISSUES

The enforcement of the contaminated site remediation, which generally includes the steps registration, risk assessment and remediation is with the 16 Federal States (Länder) of Germany. Together with the Länder regulation more than 35 lists exist all over the country containing different values for risk assessment and cleanup. In order to harmonize regulations and values the Federal Government submitted the Federal Soil Protection Act (FSPA), which has been enacted on March 1st, 1999. To complete the federal legal framework on contaminated land in Germany sublegal regulations have been laid down in an ordinance submitted later on. This Federal Soil Protection and Contaminated Sites Ordinance came into force in July 1999.

The FSPA includes precaution issues as well as remediation of contaminated soils and sites. The main purpose of the FSPA is to protect against harmful changes in the soil. Harmful changes in the soil exist when the soil functions are impaired and when this leads to danger, to considerable adversely affects for the individual or for the general public. The definition of the FSPA includes natural soil functions and functions of the soil utilization.

The two terms harmful changes in the soil and contaminated sites in the FSPA cover all burdens of the soil that causes hazards for human beings and the environment. Contaminated sites (CS) are defined as follows:

- closed-down waste disposal facilities or other estates on which wastes have been treated, stored, or disposed (abandoned waste disposal sites-AWDS); and
- estates of closed-down facilities and other estates on which environmentally hazardous substances have been handled (abandoned industrial sites-AIS), which cause harmful changes in the soil or other hazards for the individual or for the general public. Sites which are suspected to be contaminated (SCS) are by definition of this law AWDS and AIS, which are suspicious for harmful changes in the soil or other hazards for the individual or the general public.

Following regulations for the remediation of contaminated sites are a substantial part of the FSPA:

- the authorities are responsible for registration, investigation and assessment of SCS;
- authorities may require under certain conditions remedial investigations and a remedial plan by those who are obliged for remediation;
- the remedial plan should provide in the case of serious and complex CS transparency and by that provide a substantial contribution to the acceptance of the necessary remedial measures by the affected persons;
- the remedial plan should cover a summary of the risk assessment and the remedial investigations as well as the remedial goals and the remedial measures;
- by the rule the remedial plan is worked by an expert;
- in the cases of CS and SCS, responsible persons are obliged to announce these sites and to carry out self-control measures; the authorities are responsible for the supervision;
- together with the remedial plan the obliged person can submit a public contract for the remedial measures; and
- to enhance the approval procedure the official obligation of the remedial plan as well as the official order for remediation concentrates all necessary permissions from other laws.


## 2. REGISTRATION OF CONTAMINATED SITES

The registration of suspected contaminates sites (SCS) is carried out by the Federal States (Länder). Inventories of suspected contaminated sites have been set up by the Länder, however, they are based on their specific definitions and specific local regulations. Consequently, comparison of the Länder figures is only possible to a restricted extent. The focus of all Länder inventories are the numbers of abandoned waste disposal sites (AWDS) and abandoned industrial sites (AIS). These figures had been summed up to a nationwide number lately in December 1998 to more than 300,000 SCS excluding military contaminated sites and former armament production sites. More than 100,000 are AWDS and nearly 200,000 are AIS. The table with the individual figures from the Federal States is published in the 1999 annual report of the Pilot Study.

## 3. REMEDIAL METHODS IN USE

According to the definitions of the Federal Soil Protection Act remediation are measures:

- for the removal or reduction of contaminants (decontamination measures);
- that prevent or reduce the spreading out of contaminants on a long-term basis without removing contaminants (safeguarding measures); and
- for the removal or reduction of harmful changes of the physical, chemical and biological nature of the soil.

Generally, the technological standard for the treatment of contaminated soil is high. Public funding has contributed significantly to the development of soil treatment technologies. Expenses spent by the public sector for R\&D are estimated being added up to 300 million Deutsche Mark for about 200 projects within the last 20 years. Industry investments in the range of approximately 900 million Deutsche Mark have been take place only for soil decontamination. Meanwhile, there are more than 100 soil treatment plants in operation providing a total treatment capacity of almost 4 million $t / y e a r$. The technologies available for field application cover a broad range of on and off site techniques as well as in situ strategies for soil treatment by means of biological treatment, soil washing and thermal treatment. However, due to cost constraints, also safeguarding measures like encapsulations, surface sealing or excavation and disposal became more meaningful in the last few years. It is estimated that about $50 \%$ of all remedial action in Germany are done by safeguarding measures.

The decision on weather to use safeguarding or decontamination measures for remediation is a complex procedure determined by a multitude of factors (remedial investigation). The Soil Protection Act sets priority on the warding off of hazards. According to the legal framework it hardly makes difference regarding the technical procedure to reach this. From a purely environmental point of view, however, decontamination of contaminated soil is still the better option for remediation. It is an important tool to support the recycling of wastes, to protect natural resources and landfill space and thus to contribute to the principles of a sustainable development.

In this context UBA has conducted a survey on soil management in Germany arising from contaminated land. The objective was to analyze the soil streams from soil treatment plants regarding their recycling potential and their contribution to the reuse of contaminated soil. 85 soil treatment plants, out of 108 plants written to, took part in the survey; this corresponds to a response rate of approx. $80 \%$. Thus a coverage rate of approx. $65 \%$ of all the plants in Germany has been achieved which for 1997 document an input of approx. 1.8 million $t$ and an output of approx. 1.6 million $t$ (Table 1). During the period covered by the study (1993-1997) the input quantities (quantities actually treated in the plant) of the plants participating in the study rose from approx. 409,000 tons to more than 1.8 million tons. Accordingly the output also rose (soil cleaned in the plants) from approx. $341,000 \mathrm{t}$ to approx. $1,574,000 \mathrm{t}$. Of that, in 1993 approx. $335,000 \mathrm{t}$ was recycled. In $1997,1,568,000 \mathrm{t}$ was recycled. Thus the recycling rate almost
reaches $100 \%$ (Fig. 1). The figures obtained in the survey show, however, that the average degree of usage was about $60 \%$.

Table 1: Development of the capacities, treated, cleaned and recycled soil quantities from 1993 to 1997 for the soil treatment units covered by the study

|  | $\mathbf{1 9 9 3}$ <br> $(\mathbf{t} / \mathbf{a})$ |  | $\mathbf{1 9 9 7}$ <br> $(\mathbf{t} / \mathbf{a})$ |
| :--- | :---: | :--- | :---: |
| Industrial capacity | $1,460,800$ | $===>$ | $3,224,700$ |
| Soil accepted | 539,120 | $===>$ | $1,843,030$ |
| Plant input | 408,586 | $===>$ | $1,791,890$ |
| Plant output | 341,396 | $===>$ | $1,574,287$ |
| thereof recycled | 335,306 | $===>$ | $1,567,610$ |



Figure 14: Recycling rate for all soil treatment measures

## 4. TECHNOLOGY DEVELOPMENT PROGRAM/RESEARCH AND DEVELOPMENT ACTIVITIES

The technology development program, which is mainly funded by the Federal Ministry for Education and Research (BMBF), is executed by the BMBF Project Management Agency for Waste Management and Remediation of Contaminated Sites within the Federal Environmental Agency (UBA). The high standard of available soil treatment facilities being reached in Germany (see above) is particularly due to the funding policy of the BMBF in the past.

This, of course, is also the reason that the focus for future research and development moved to optimizations of available solutions in terms of cost-effective technologies and strategies. In this context mainly bioremediation techniques for soil, groundwater treatment walls including permeable reactive barriers and natural attenuation strategies have to be mentioned.

A Joint Research Group, Processes for the Bioremediation of Soil, comprises seven joint projects with more than 30 single projects. This interdisciplinary group is working on the development of innovative processes for the bioremediation of contaminated soils. After the laboratory phase, not only their effectiveness is tested under application-oriented conditions, but also their success is monitored by a complex control system that goes far beyond a conventional chemical analysis of pollutants. A comprehensive handbook on the results will be published within this year.

Currently starting is a joint research project on the "Application of Treatment Walls for the Remediation of Contaminated Sites." Proposals for 38 single projects have been submitted to UBA for evaluation. A committee of experts (chair: Harald Burmeier) has selected about 10 research projects on this subject for funding within the next two years. The financial contribution of the BMBF will be in the range of 10 million Deutsche Mark. They cover a broad range of application purposes and technological principles. The final objective of the joint research project is the elaboration of a handbook on the selection, design and planning of permeable treatment walls to be used by consultants and administration.

A further joint research project is currently under final preparation. Based on an announcement by the BMBF universities and consultants have been requested to submit proposals for research projects in the field of monitored natural attenuation. Deadline for the call was the end of April 2000. At this date 212 proposals have been submitted. They will be further evaluated for final funding by a committee of experts that is currently being set up. It is expected that about 50 projects will be funded as part of this joint research project for a period of five years. The total amount of public funding is estimated to 50-60 million Deutsche Mark. The focus on the intended research activities regarding natural attenuation will be in the following fields:

1. Mining and smelting
2. Refineries and tank storage facilities
3. MTBE
4. Gas work sites
5. Chemical and textile industries, arsenic
6. Landfills and dump sites
7. Abandoned Armament Sites
8. Military sites
9. Agricultural Sites
10. Sediments

The main objectives of the project are:

1. Identification of frame conditions for economic and environmental useful self-cleaning processes (Note: Within the scope of the project the term "Natural Attenuation" is considered to encompass both, dilution and reduction processes like absorbtion and/or degradation of pollutants in soil or groundwater
2. Identification of substances that can be accessed by natural attenuation or enhanced natural attenuation
3. Assessment of the behavior of pollutants in soil or groundwater regarding natural self cleaning processes
4. Requirements on soil and groundwater schemes regarding the application of natural attenuation
5. Design and conduction of long term monitoring measures to quantify the reduction of contamination and to predict the long-term behavior of the contamination under the aspects of future use options.

The joint research project on natural attenuation is desired to start in late summer 2000.

## 5. CONCLUSIONS

With the enactment of the Federal Soil Protection Act and the Federal Soil Protection and Contaminated Sites Ordinance, Germany has for the first time a comprehensive legal framework to deal with contaminated land. Registration of contaminated sites and research and development of remediation
technologies are also far advanced. Thus, contaminated land management in legal and technical terms will become more in the focus of enforcement than of research and development in the future. However, experiences with the enforcement and execution of the legal framework will be vital over the next few years for further optimizations.

Nevertheless, the contaminated land problem is far away from being solved in Germany. The legal framework and the availability of remediation technologies are undoubtedly essential tools to overcome the environmental risks. But they are not specifically designed to promote site redevelopment in terms of attracting new investors for new uses. Thus, future activities in Germany will focus on the development of new strategies and economic instruments for bringing the land really back into beneficial use under urban planning aspects. Brownfield redevelopment in the context of legal, environmental, social, urban planning and economic issues will be the wider context of contaminated land activities in the future.
Actually, UBA is involved in a couple of national and international activities so far. Especially, the ongoing international co-operation of the UBA led working group 1 "Brownfield Redevelopment" as part of EU funded Concerted Action CLARINET made quite clear that brownfield is a subject of international concern.

## 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 for soil quality, there are several components in Greek law that 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 (JMD 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 waste 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 semivolatile 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:

1. In situ chemical stabilisation of heavy metal polluted soils
2. Removal of heavy metals from contaminated soils by chemical extraction techniques
3. Bioremediation of soils contaminated by heavy metals and metalloids
4. Remediation of polluted ground waters using permeable reactive barriers

## ITALY

## 1. LEGAL AND ADMINISTRATIVE ISSUES

### 1.1 Legal Background

The first legal provision for the assessment and remediation of contaminated sites in Italy dates back to the Environment Ministry Decree (DM) of May 16th 1989. This law established the general guidelines for drawing up regional plans for contaminated sites assessment and management according to the following processes:

- identification of potentially contaminated sites
- evaluation of the level of contamination
- definition of priority sites to be cleaned on a short-term basis
- definition of priority sites to be cleaned on a mid-term basis

From early 90's a number of regions elaborated own technical regulations relating to contaminated sites characterization and assessment, setting soil quality standards and application of cleanup technologies. Criteria for site-specific assessment of risks were envisaged. Several regions compiled regional remediation plans and in 1997 preliminary results were summarized on a national basis.

The legislation relevant to contaminated sites has been recently detailed and expanded: by the beginning of 1997 the Waste Act (D. Lg.vo 22/97) was adopted; this law provided the institutional framework for contaminated sites assessment and management, and established the requirements for the development of the technical and administrative procedures relevant to contaminated sites inventory, characterization and assessment, cleanup, safety measures and monitoring (Art. 17). The norm contains provisions on the administrative procedures for site decontamination and remediation and on the necessary steps to bring concentration of pollutants within legally binding limits. Art. 17 also sets obligations for the person responsible for a case of contamination to clean it up, and provides for sanctions on the violation of administrative duties. In cases of difficult or impossible liability definition or in case of negligence from the polluter, the public authority, municipality or region takes care of safety actions and site remediation. Public cleanup represents a legal binding restrain of the area. The public authority keeps ownership privileges on the site until costs of remediation are recovered from the responsible party or site owner. The public authority can initiate legal actions to recover costs from the polluter or site owner.

Cleanup operations represent a "real burden" placed on the site to be decontaminated, which results from the "site destination certificate" and which follows the site also when it is transferred to a different owner. The only way to remove the burden will be to clean up the contaminated site.

Another major step in legislation was the enforcement of Law 426 of December 9, 1998 that established a first list of sites of national interest that deserve special attention for environmental, economical and social reasons, and are object of direct involvement and funding from the government. The Ministry of the Environment together with the ANPA (National Agency for the Protection of the Environment) together with other competent national and local institutions are responsible for approving and issuing permits relevant to site investigation, assessment and remediation projects. ANPA has the task to define (comparative) risk based criteria to establish the inventory and priorities for actions on sites of national interest.

The list includes major industrial poles, partly or entirely dismissed. The law assigns public funds for the remediation of those sites and direct government responsibility, through the Ministry for the Environment, the National and Regional Environment Agencies together with other technical institutions that have the task to issue the permits for characterization, for preliminary and final remediation projects
or directly plan remedial actions in case of owner negligence. In some cases projects are carried out according to agreements between stakeholders and control bodies.

Technical and more specific administrative guidelines have been then adopted with Environment Ministry Decree (DM) 471 of October 25, 1999, which is actually the "implementation decree" of Art. 17 of D.Lg.vo 22/97. The decree provides:

- definition for contaminated and potentially contaminated sites, emergency and permanent safety measures, cleanup and cleanup with safety measures, environmental restoration;
- polluter and site owners obligations for site registration and cleanup;
- criteria and administrative procedures to be followed by site owner to carry out characterization and remediation projects;
- tasks of the different local administrative levels: municipality, province, region;
- definition of acceptable contaminant limits for soil (two land use categories), surface water and groundwater for approximately one hundred chemicals;
- criteria for soil and water sampling and analysis;
- criteria for site investigation and remedial actions design, together with stepwise licensing procedures.


### 1.2 General Principles and Definitions

A site is defined contaminated, and registered as such, when even only one chemical exceeds the acceptable limit concentration (limit values) in soil for the specific land use, surface water, or groundwater. A site is defined as potentially contaminated when, because of actual or historic activities, a potential exists that concentrations of polluting chemicals in soil, groundwater or surface water, may determine a hazard to public health or the environment.

- Whenever limit values are exceeded, or an actual risk exists that it can be exceeded, local authorities must be informed and cleanup or safety actions have to be taken on the site to remove sources of pollution and remove or reduce pollution in the environmental media within limit values.
- Cleanup is defined as the remedial action that removes pollutants or reduces their concentrations to a level equal or below limit values.
- Emergency safety measures are urgent interim actions to remove polluting sources, to contain their diffusion and to prevent contact with the sources themselves.
- Cleanup with safety measures is an integration of actions to reduce concentrations to residual concentrations higher than limit values together with safety and monitoring measures. This applies when best available technologies at affordable costs show that legal limit values, for the specific land use destination, cannot be reached as cleanup targets. Under these circumstances, site-specific residual concentrations in soil or groundwater are accepted, as long as a site-specific risk assessment, demonstrates that they are protective of human health and the environment.
- Permanent safety measures are meant as long-term isolation actions to confine polluting sources on site, when best technologies at affordable costs show that sources cannot be removed.
- $\quad$ Site-specific risk assessment guidelines are described within the remediation design steps. Sites treated under a risk assessment procedure, i.e., when generic limit values are not reached, need additional safety measures and are not considered thoroughly cleaned up.
- The general principle that in-situ techniques, rather than digging and landfilling techniques, must be encouraged, is established.


## 2. REGISTRATION OF CONTAMINATED SITES

Preliminary inventory data, on the basis of the Regional plans completed after DM of 1989, for potentially contaminated sites, accounted for about 9000 sites from 14 out of 20 regions. 1200 sites were assigned a short and mid term priority class for remediation.

The more recent laws distinguish between "census" (censimento) of potentially contaminated sites and "register" (anagrafe) of contaminated sites. DM 471/99 defines criteria and procedures for registration of contaminated sites.

### 2.1 Procedures for Registration of Sites

Three different procedures are envisaged to register and to initiate actions on contaminated sites:

1. a notice that is communicated to local authorities from the polluter;
2. an ordinance that is issued by controlling authorities;
3. 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 (Art. 7).

Tasks and powers of local authorities and competent institutions in issuing ordinances to parties responsible of pollution are defined under procedure 2. (Art.8). Ordinances are issued by competent Municipality.

For procedure 3., which requires a formal registration of the site to local authorities, the deadline has been established within current year 2000. Registered contaminated sites will be included in regional registers that will have to be drawn up and completed by the end of year 2000. Regions will decide about priorities of actions according to criteria formulated by the ANPA.

### 2.2 Procedures for the Implementation of Remedial Actions

Administrative steps and technical requirements for preparing and authorizing projects of remedial actions are defined: Three sequential project levels have to be followed (Art. 10):

1. a characterization plan
2. a preliminary project
3. a final project

Particular projects have to follow also EIA procedures and comply with the relevant legislation to obtain the specific permit. Financial warranties, not lower than $20 \%$ of estimated remediation costs, are provided to the competent Regional administration as an engagement for correct execution and completion of the remediation project.

Owners of a plurality of sites may stipulate special agreements for stepwise remedial programs with local and central authorities.

After completion of site cleanup, certification and compliance monitoring is duty of the Province authority.

Remedial projects relevant to polluted soil volumes less than $100 \mathrm{~m}^{3}$ and cleanup projects not requiring safety measures and no EIA procedures, are not subject to the formal licensing procedure described above.

General criteria for the choice and implementation of cleanup and containment actions are given. In situ and on site methods are encouraged together with the reuse of off-site treated soils. Solutions that reduce long-term control and monitoring needs are privileged. Proposed innovative technologies must be tested in laboratory experiments and verified in pilot tests. Provisions are provided for the use of GMOs in bioremediation projects.

## 3. TECHNOLOGY DEVELOPMENT PROGRAM AND REMEDIAL METHODS IN USE

There is no specific national program for technology development. Several initiatives have taken place on a case-by-case basis. Development of innovative technologies initiated after decree of 1989 and after enforcement of regional laws in the following years.

Several remediation technologies have been applied in the past, but a comprehensive statistics of completed cases is not available. A summary of methods implemented by major companies operating in the country follows:

Summary of methods and number of applications completed by six major companies (more than one method might have been applied at the same site):

| Remedial techniques | Number of applications | \% |
| :--- | :---: | :---: |
| Static containment (capping, impermeable <br> barriers, landfilling) | 205 | 54.3 |
| Hydraulic containment | 36 | 9.5 |
| Dual phase extraction | 49 | 13.0 |
| Soil vapor extraction, Soil venting | 89 | 23.6 |
| Bioventing, In situ Bioremediation, Air sparging | 72 | 19.1 |
| Biopile | 9 | 2.4 |
| Landfarming | 17 | 4.5 |
| Thermal desorption | 3 | 0.8 |
| Soil washing | 3 | 0.8 |
| Immobilization | - | 0.5 |
| Incineration | 1 | 0.5 |
| Reactive barriers | 3 | 0.8 |
| Natural attenuation | 4 | 1.1 |
| Total | 377 | 100 |

## 4. RESEARCH AND DEVELOPMENT ACTIVITIES

The largest program for research and development of remediation technologies has been launched by the Ministry for Scientific and Technological Research under National Research Program n. 15 (PNR15). Main contractor is AREA; partners are the Center for Environmental Research Montecatini, the University of Bologna and the Institute for Cancer Research. The program started in 1997 and is expected to last till end of 2001. Funds provided for the program are approximately 6,5 million euros. The program includes the following subprograms:

- R\&D for bioremediation techniques in-situ and on-site
- $R \& D$ for vitrification techniques in situ
- training courses

A number of other individual research projects are being considered by the Ministry for the Environment and others are presently funded by the Ministry for Scientific and Technological Research and by the ANPA.

Bioremediation and phytodepuration deserve particular attention. One research project aims at integrating phytodepuration and biodegradation processes in order to achieve synergic effects for the degradation of PCBs and PAHs in soil.

Other research activities on technology development are carried out within international and EU funding programs or by research investment and by specific initiatives from the national holding for hydrocarbons. One important EU funded project (under ESPRIT program) deals with the implementation of models to simulate bioremediation processes in contaminated soils.

From a wider point of view other research projects have been carried out and are still ongoing for the development of:

- risk assessment methodologies for contaminated site management
- decision support systems for risk assessment
- ecological risk assessment of soil and sediments
- remote sensing investigation methods


## 5. CONCLUSIONS

National procedures and technical requirements for remediation of contaminated sites have been enforced very recently in Italy. Established provisions for legally binding and stringent acceptable contamination limits, together with economic considerations, may perhaps hinder the application of several remediation technologies. In this frame, site-specific risk assessment may have a critical role.

Criteria for registration of contaminated sites have also been established recently and it is perhaps too early to comment on their efficacy in the definition of the real dimension of the contaminated sites problem.

Even though wide national research programs have not been formulated yet, it is already evident that the new legislation will provide a strong impulse to the development of new technologies.

## JAPAN

## 1. LAW CONCERNING SPECIAL MEASURES AGAINST DIOXINS

In Japan, dioxin pollution has been the serious social problem because high concentrations of dioxins ( $8,500-52,000,000 \mathrm{pg}-\mathrm{TEQ} / \mathrm{g}$ ) have been detected in soils around the incineration facility of municipal solid waste. In response to this concern, the Law Concerning Special Measures against Dioxins was promulgated on July 16, 1999, and enforced on January 15, 2000.

Dioxins may cause serious effects on human life and health. Thus, this law has established the necessary environmental standards, emission regulations and control measures (particularly for soil contamination) in order to attempt the removal and prevention of the environmental pollution by dioxins. "Dioxins" are defined as polychlorinated dibenzofurans, polychlorinated dibenzo-para-dioxins, and co-planar polychlorinated biphenyls.

### 1.1 Soil Pollution Control Measures under the Law Concerning Special Measures against Dioxins

Under the Law Concerning Special Measures against Dioxins, the Government shall establish Environment Quality Standard, and the prefectural governors shall monitor and survey the pollution of the soil caused by dioxins periodically.

As a result of monitoring and surveillance, prefectural governors shall be able to designate as the controlled areas against soil contamination by dioxins, i.e., the area where the level of soil contaminated by dioxins fails to comply with Environmental Quality Standard, and where is accessible to citizens. After designating controlled areas, prefectural governors shall, without delay, establish Plans of Measures against Soil Contamination by Dioxins, and conduct the removal and reduction of dioxin-derived risk.


Figure 1: Scheme for implementation of soil pollution control measures under the Law Concerning Special Measures against Dioxins

The provision of the Pollution Control Public Works Cost Allocation Law shall be applied to projects based on the Plans of Measures, when the causal relation based on scientific knowledge is clear between the discharge of dioxins by a business establishment and contamination by dioxins. All or a part of the cost which is necessary for the measures can be charged to cause persons.

And the provision of Law Concerning Special Government Financial Measures for Pollution Control Projects shall be applied to the control measures, i.e., the measures conducted by local government will be subsidized by the national government.

### 1.2 Environmental Quality Standard

The Environmental Quality Standard of dioxins in soil was established as $1,000 \mathrm{pg}-\mathrm{TEQ} / \mathrm{g}$ or less (Environment Agency Announcement No.68, 1999). The Survey Guideline Criterion in which additional detailed surveys should be required from the viewpoint of prevention of progress of the pollution was also established as $250 \mathrm{pg}-\mathrm{TEQ} / \mathrm{g}$ or more. The Environmental Quality Standard has been set to generally apply to all soils except for the soil of where waste landfills, and other facilities distinguished appropriately from the general environment.


Figure 2: Environmental Quality Standard and Survey Guideline Criterion

This Environment Quality Standard was established through evaluation of the exposure from soil. There are the following possible exposure pathways for the dioxins in soil to be transferred into the human body.


Figure 3: Exposure pathway of dioxins to human populations from soil start points
In the process for calculating to estimate the exposure from soil, "direct ingestion" and "direct skin contact" were considered. The average daily exposure over a lifetime can be represented by the following expression:
(Average daily exposure over a lifetime)(pg-TEQ/kg/day)= (child's daily exposure) $\times 6$ (adult daily exposure) $\times($ exposure period 6$) / 70($ years $) \times 50(\mathrm{~kg})$
a) Exposure from ingestion
(soil concentration) $\times($ daily quantity of soil ingestion $) \times($ absorption rate $) \times($ frequency of exposure)
Daily quantity of soil ingestion: child $200 \mathrm{mg} /$ day, adult $100 \mathrm{mg} /$ day
Absorption rate: 25
Frequency of exposure: 1 (everyday)
b) Skin exposure
(soil concentration) $\times($ contact quantity per unit area) $\times($ surface area of skin $) \times($ absorption rate $) \times($ frequency of exposure)

Contact quantity per unit area: $0.5 \mathrm{mg} / \mathrm{cm}^{2}$
Surface area of skin: child $2,800 \mathrm{~cm}^{2}$, adult $5,000 \mathrm{~cm}^{2}$
Absorption rate: 1
Frequency of exposure: 0.6 (fair weather ratio) $\times$ [child $7 / 7$ (everyday), adult $2 / 7$ (weekend)]
Assume a soil concentration of $1,000 \mathrm{pg}-\mathrm{TEQ} / \mathrm{g}$, calculating the exposure to dioxins from soil gives an estimate of $0.31 \mathrm{pg}-\mathrm{TEQ} / \mathrm{kg} / \mathrm{day}$. In considering the exposure from diet and atmosphere in the same way as TDI (Tolerable Daily Intake: $4 \mathrm{pg}-\mathrm{TEQ} / \mathrm{kg} /$ day), it is probably appropriate to use $1,000 \mathrm{pg}-\mathrm{TEQ} / \mathrm{g}$ as the Environmental Quality Standard value at which measure action should be implemented.

### 1.3 Monitoring and Surveillance

Prefectural governors shall, in consultation with the heads of local administrative agencies of the national government and heads of local governments, conduct surveys and measurements of the status of pollution of the soil caused by dioxins in the areas under the jurisdiction of the prefecture concerned.

The scheme about the monitoring and survey is as follows.
a) Regional Survey

Ambient Soil Survey: Surveys not to think about the influence of a specific source of emission in advance and to grasp the conditions of the pollution of the general environment widely.

Emission Source Surrounding Survey: Surveys to grasp the influence of a source of emission
Site Assessment Survey: surveys to grasp the conditions of the area with fear of the pollution by dioxins
b) Detailed Survey

Surveys to confirm the conditions of the circumference area for the sampling point of 250 pg TEQ/g or more
c) Contaminated Area and Depth Identification Surveys to identify the area and depth of the soil more than $1,000 \mathrm{pg}-\mathrm{TEQ} / \mathrm{g}$
d) Evaluation of Measures

Surveys to confirm the effect after measures such as the removal of the pollution were conducted
e) Continuous Monitoring

Surveys to carry out after 3-5 years to grasp the change of the concentration of dioxins in the soil


Figure 4: Scheme of surveys for soil contaminated by dioxins

## 2. REMEDIATION TECHNOLOGIES FOR DIOXIN-CONTAMINATED SOIL

The Environment Agency of Japan invited submissions on 28 May 1999 for ideas on practical technologies that are safe and reliable for purification of soil contaminated with dioxins. Within about one month 48 , submissions were received.

The Investigative Panel on Remediation Technologies for Dioxin-Contaminated Soil (Chairperson: Dr. Masaaki Hosomi, Professor of Tokyo University of Agriculture and Technology) was established for the purpose of investigating methods of remediation. As a result of examination, the following two methods were selected as demonstration technologies which can be proven in the field, based on criteria such as soundness of theory, safety and efficiency of purification. Testing of these methods is now being discussed with interested local governments.

Table 1: Demonstration Technologies That Can Be Proven in the Field

| Method | Principle |
| :--- | :--- |
| In Situ Vitrification Method | An electrode is placed in a container in the ground, which <br> holds contaminated soil. Electricity is passed through the <br> electrode, generating heat $\left(1,600-2,000^{\circ} \mathrm{C}\right)$ that brings the soil <br> to a molten state and thermally cracks organic compounds <br> such as dioxins into safer substances such as carbon dioxide. <br> Gases such as carbon dioxide produced by thermal cracking <br> of organic compounds are collected in a cover and <br> decomposed by a thermal oxidizer at more than $850^{\circ} \mathrm{C}$. |
| Base Catalyzed <br> Decomposition Method | Safe alkali reagents (sodium bicarbonate) are added to and <br> mixed with contaminated soil. Soil is detoxified by <br> dechlorination of dioxins in the soil by heating at 350 to <br> $400^{\circ} \mathrm{C}$ in a soil reactor like rotary kiln. The small amounts of <br> gaseous dioxins, which are not dechlorinated in a soil reactor <br> are collected in a condensation unit. The liquid containing <br> dioxins is then rendered harmless by adding alkaline reagents <br> and heating at over $300^{\circ} \mathrm{C}$ in a liquid BCD reactor. |

The following four technologies were also selected as seed technologies, since they are at the final stages of development. These technologies are considered likely to find practical applications quickly and are suitable for small-scale testing. At the next NATO/CCMS meeting, the experimental result s for demonstration and seed technologies will be introduced.

- Supercritical Water Oxidation Method
- Mechano-chemical Method
- Vacuum Thermal Cracking Method
- Bioremediation Method


## LITHUANIA

## 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) 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 are limiting use to minimum application rates.


Figure 1: Total Usage of Nitrogen, Phosphorus and Potassium Fertilisers in Lithuania (19861996)

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 $100 \mathrm{~m}^{2}$ (a workshop) to almost 14000 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 <br> (ha) | Distribution according <br> to the damage type <br> $(\%)$ |
| :--- | :---: | :---: | :---: |
| 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 | $\mathrm{p} / \mathrm{p}^{*}$ | 2 |
| Radioactivity | 9 | $\mathrm{p} / \mathrm{p}$ | 0,2 |
| Rocket propellant | 20 | $\mathrm{p} / \mathrm{p}$ | 1 |
| Explosives | 12 | $\mathrm{p} / \mathrm{p}$ | 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 10000 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 $1 \mathrm{~m}^{3}$ 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:

- Hazardous Substances: Maximum Permitted and Temporary Permitted Concentrations in Soil. Hygiene Norm - HN 60-1996.
- Recommendations for Evaluation of Soil Chemical Contamination, 1997.
- The Maximum Permitted Level of Oil Products in the Upper Lithosphere (Ground) Layer - LAND (Lithuanian Environmental Normative Document) 12-1996.
- 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

## 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 EURO. The Netherlands is now spending about 0.5 billion EURO 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 cleanup on the basis of suitability for use. At the same time, the government proposed other changes to soil protection legislation, including greater devolution of responsibility for cleanup 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 cleanup. 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 that is needed to initiate and stimulate the measures that are best suited to the local situation (tailor-made solutions).

With these measures, the Dutch government wants to achieve ambitious objectives. 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 was 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: 1) anyone intending to excavate and to move soil for building activities, has to report the quality of the soil to provincial authorities; and 2) 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 (EURO) |
| :--- | :--- | :---: |
| 1980 | 350 | 0.5 billion |
| 1986 | 1,600 | 3 billion |
| 1999 | 110,000 | $15-25$ billion* |

* based on new policy


## 3. REMEDIAL METHODS [1]

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. [1]

## 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 topsoil and the subsoil. In the approach to the topsoil, 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:

1) via a standard approach per case or cluster of cases. By this means the decision-making may be simpler.
2) 2) via custom-made work per case or cluster of cases. This is obvious if the standard approach offers no solutions.
1) 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."

## Top soil

In the standard approach for the topsoil 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 that 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.

## 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 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 behind in the soil in many cases. Therefore, care is required. This care may consist of registration (establishment), monitoring (measuring), and 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 cause 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 cost savings of $35-50$ percent could 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 percent by the new standard approach;
- approximately 10 percent by cleaning and draining off less contaminated groundwater;
- approximately 5 percent by custom work per area.

Monitoring will show the extent to which the cost reduction will be achieved.

## Decision-Making

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 licenses "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

Starting January 1, 1999, most of the research on contaminated land is organised in one centre: The Centre for Soil Quality Management and Knowledge Transfer (SKB). The SKB is a cooperative 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 transfer 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 BEVER, i.e., functional remediation and cost-effective contaminant removal.

A decisive approach to soil contamination and the development of new forms of co-operation must put an end to the stagnation that hampers the optimal use of the little space available in the Netherlands. The SKB wants to achieve this not only through smarter and cheaper technical solutions, but also by devoting
attention to managerial processes, rules and regulations, planning and, last but not least, communication. This requires applying existing knowledge on the one hand and developing knowledge via applied and strategic/fundamental research on the other.

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 gasworks sites.


## Restructuring natural areas

Nature development and redesignation of agricultural areas in combination with the remediation of former dumpsites 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.

## $\underline{\text { Maintenance and soil management }}$

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.

A Supervisory Board is responsible for the policy and officially takes all decisions. Important decisions concern the direction in which the programme will be developed, long-term plans, annual action plans, and the budget. All parties involved in soil management are represented in the board, namely the ministries of VROM (Housing, Planning Environment), LNV (Agriculture, Nature Management and Fisheries), V\&W (Transport and Public Works), Defence, OC\&W (Education and Science) and EA (Economic Affairs).

The demand side of the market includes trade and industry, provincial and municipal authorities, water boards and managers of rural areas. The supply side of the market includes trade and industry, consultants, knowledge institutions and universities. Other relevant parties are funding organisations, property developers, environmental groups, insurance companies and branch organisations.

The SKB is organised as a demand-driven body for the development and transfer of knowledge. This implies that the organisation does not determine the activities itself, but rather formulates the demand for knowledge and the supply of solutions and avenues for solutions with the interested parties.

The SKB is financed by government (18 million EURO) and by the public private market ( 8 million EURO) for 4 years: 1999-2002.

As of June 2000, about 50 projects have been started; only some has been completed.

## 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 costeffective 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 (June 2000) about 50 on-going projects.

## NORWAY

## LEGAL AND ADMINISTRATIVE ISSUES

The Pollution Control Act from 1981 is the main law regulating the cleanup 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 landowner may be held liable for investigations and remedial actions.

The Pollution Control Act gives the authorities a very strong legislative tool for cleanup of contaminated land. Consequently industrial companies may be held responsible for historic contamination that occurred before they took over the site or on their property before contaminated soil was regulated (i.e., before the 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-bystep approach where alternative and site-specific acceptance criteria can be generated and also allows qualitative methods.

Two simple computer applications are available as Excel spreadsheets and on the Internet at the following addresses: http://www.risiko-forurensetgrunn.ffi.no and http://www.miljoringen.no. They will also be available on SFTs homepage 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 cleanup of contaminated land in October 1999. These are:

- The most seriously contaminated sites shall be cleaned by end of 2005 (about 100 sites) decisions on investigation and cleanup on the secondly most contaminated sites by end of 2005 ( 500 sites).
- Investigations and cleanup will be carried out and paid for by private 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.

For further information please see tour de table abstract from 1999.

## SLOVENIA

## 1. INTRODUCTION

June 25, 2000, marked exactly nine years since the Republic of Slovenia seceded from the Federation of Yugoslavia to become an independent state. Among other consequences of this historic occasion, Slovenia had to rapidly establish its own comprehensive legal and state administration systems to replace the former Yugoslavia systems, which had been far less specific to the needs of Slovenian citizens and their wider environment. Such systems were needed to underpin freedom and democracy and support the flowering of modern life in the newly independent state-of the kind that Western European countries had been able to establish much earlier.

Protection and enhancement of the environment was an important part of this new focus, which was also underwritten by the Constitution. Indeed, the previous political and economic systems had resulted in the serious neglect of the environment. At the end of the 1990's much hope had been put on the Zeleni movement (the Greens) to help improve the focus on the environment. The only environmental movement allowed under the former Yugoslavia system, the Zeleni were quite well supported by ordinary people. In the first democratically elected Slovenian government the Green movement had considerable influence, with representatives in many important positions. For example, included in the Slovenian State Presidency of four was one representative from the Greens. The movement also had a vice president in the government as well as four ministers while in the National Assembly there were more than ten deputies plus a vice-president.

The Green movement supporters were hopeful that there would be a new emphasis on achieving positive results for the environment. But despite the high expectations, actual results have been very disappointing-the Greens have turned out to be much more interested in preserving their well-paid positions than preserving and enhancing the environment.

So it followed, in the 1992 elections the Greens won only a few seats in the National Assembly and had just one minister who soon resigned. The incumbent Minister for the Environment and Physical Planning had previously been a member of the Green movement but changed parties a few months before the elections to help keep his ministerial position. With all this, the Zeleni movement and political party practically collapsed and by the start of 1994 a Liberal Democrat MP became minister, even though that party had previously shown little concern for the environment.

## 2. SUMMARY OF ENVIRONMENTAL PROTECTION LEGISLATION ADOPTED AND AMENDED SINCE INDEPENDENCE

The legislation drawn up and adopted over the last nine years includes the so-called "umbrella" acts from which specific regulations governing individual areas have been adopted. The most important umbrella act has undoubtedly been the Environmental Protection Act (Ur.l. RS, no. 32/1993). From this act, a total of eighty decrees and twenty-seven regulations, orders and instructions governing individual areas have been adopted, as follows:

- 64 decrees, regulations, orders and instructions concerning water (discharges into water, protection of water, etc.);
- 16 decrees and regulations dealing with protection of the atmosphere, gas emissions into the atmosphere, etc;
- 4 decrees and instructions dealing with waste, the most important of which are the two implementation acts: the Regulation on Waste Management (Ur.l. RS, no. 84/1998) and the Regulation on Waste Disposal (Ur.l. RS, no. 5/2000); and
- 23 decrees and other implementation acts dealing with other areas of environmental protection (disposal of toxic substances into the soil, etc).

Another extremely important act adopted last year was the Chemicals Act (Ur.l. RS, no. 36/1999) which, coupled with five implementation acts, comprehensively governs this area of extreme sensitivity for the environment. This legislation has been drawn up in accordance with EU directives.

Below is a chronological list of the legislation adopted since 1993:

## 1993

Environmental Protection Act
Decree on the Founding and Appointing of the Environmental Protection Board
Decree on Temporary Restriction of Use of Water from Water Courses
Decree on the Protection of Endangered Animal Species
Decree on Methodology for Drawing Up Opening Balance Sheets
Forestry Act
Commercial Public Services Act
Urban and Environmental Planning Amendment Act

## 1994

Decree on Limit Values, Alert Thresholds and Critical Emission Values for Substances Emitted into the Atmosphere
Decree on the Emission of Substances into the Atmosphere from stationary sources of pollution, heating plants, from waste incinerators and during the incineration of waste, from aluminum production plants, from plants for the production of ceramics and brick products, from cement production plants, from the processing of light alloys, ferrous alloys and steel, from stationary internal combustion engines and stationary gas turbines, from heat-galvanising plants, from lacquering plants, from plants for the production and processing of wood products, from plants for the production of lead and alloys from secondary raw materials
Decree on the Prohibition of the Sale and Import of Vehicles without Catalytic Converters Decree on the Management of Infective Wastes which Appear in the Performance of Health Care Activities
Decree on the Protection of Wild Fungi
Statute of the Ecological Development Fund
Decree on Concession for Commercial Exploitation of Ground Drinking Water from the Source by the Nemiljščica Stream and Prošèek Stream in Kneške Ravne
Decree on Temporary Declaration of the Škocjan Cave as a Nature Reserve - Fund for Financing
Disassembling the Krško Nuclear Power Plant and the Its Radioactive Waste Disposal Act
Organisation and Field of Work of Ministries Act
Local Self-Administration Act

## 1995

Decree on the Quality of Liquid Fuels with Respect to Sulphur, Lead and Benzene Content
Decree on Noise in the Natural and Living Environment
Decree on Noise Owing to Road and Railway Traffic
Decree on Water Pollution Tax
Decision Determining the Amount of Tax per Unit of Water Pollution for 1995
Decree on the Prohibition of Driving Vehicles in the Natural Environment
Decree on Concessions for the Commercial Exploitation of Water of the Individual Sections of 26 water Courses for Breeding Salmonidae Fish
Decree on Concessions for the Commercial Exploitation of Water of the Individual Sections of 26 Water Courses for the Generation of Electricity
Decree on Concession for the Commercial Exploitation of Water Sources in the Republic of Slovenia for Supplying Drinking Water

## 1996

Decree on Electromagnetic Radiation in the Natural and Living Environment
Decree on Tax for Atmosphere Pollution by Carbon Dioxide Emission
Decree on the Limit, Warning and Critical Emission Values of Toxic Substances in Soil
Decree on Input of Toxic Substances and Plant Nutrients into the Soil
Regulations on the Types of Activity for which an Environmental Impact Assessment is Mandatory
Decree on the Emission of Substances in the Drainage of Wastewater from Facilities and Plants for the
Production of Leather and Fur
Decree on the Emission of Substances in the Drainage of Wastewater from Plants and Facilities for the Production, Processing and Treatment of Textile Fibre
Decree on the Emission of Substances in the Drainage of Wastewater from Municipal Wastewater Treatment Plants
Decree on the Emission of Substances in the Drainage of Wastewater from Facilities and Plants for the Production of Metal Products
Decree on the Emission of Substances and Heat in the Drainage of Wastewater from Pollution Sources Regulations on Toxic Substances Which May Not be Released into Water
Decree on the Concession for the Exploitation of Forests Owned by the Republic of Slovenia
Regulations on Initial Measurement of Noise and Operational Noise Monitoring for Sources of Noise and on Conditions for Their Execution
Regulations on Initial Measurements and Operational Monitoring of the Emission of Substances into the
Atmosphere from Stationary Sources of Pollution and on the Conditions for their Execution
Regulations on Initial Measurements and Operational Monitoring for Sources of Electromagnetic
Radiation and on Conditions for their Execution
Regulations on Initial Measurements and Operational Monitoring for Wastewater and on Conditions for
Their Execution
Decree on the Conditions and the Procedure for Obtaining Authorisation for Preparing Reports on
Environmental Impact
Decree on the Export, Import and Transit of Wastes
Instructions on the Methodology for Preparing a Report on Environmental Impact
Statute of the Ecological Development Fund of the Republic of Slovenia
Škocjanske Jame Regional Park Act

## 1997

Decree on Asbestos Emission into the Atmosphere in the Drainage of Wastewater
Decree on the Tax Return Form for the Drainage of Technological Wastewater
Regulations on Operational Monitoring in Input of Toxic Substances and Plant Nutrients into the Soil
Decree on Handling the Substances Causing the Depletion of the Ozone Layer
Regulations on Procedures and Conditions for Using the Ecological Development Fund of the Republic of Slovenia Funds
Ordinance on Prices for Charging Work and Tasks of the Water Management Public Service

## 1998

Decree on Concessions for the Commercial Exploitation of Water from the Meža Watercourse for Additional Snow-making in Črna na Koroškem Ski Trail, the Črnovški Potok Watercourse for Additional Snow-making in Stari Vrh Ski Trail, and from Underground Water Wells in Čezsoča..., Šujica pri Horjulu, Dobruša pri Mošnjah for Breeding Salmonidae Fish
Statute on Treating Waste
Decree on the Form of the Report on Periodical or Permanent Measurements within the Operational Monitoring of Wastewater
Regulations on Management of Waste Oils
Instructions on the Methodology for the Formation of Prices for Compulsory Local Public Services for Municipal Waste Management and Disposal of Municipal Waste Remains

## 1999

Preservation of Nature Act
Decree on Prohibition against Alarming Protected Bird Species in the Cliffs in the Karst Margin
Decree on Temporary Declaration of the Soča River and its Tributary for Nature Reserve
National Programme for the Protection of the Environment
Decree on the Emission of Toxic Halogenous Hydrocarbons in the Drainage of Wastewater
Decree on the Emission of Cadmium in the Drainage of Wastewater
Decree on the Emission of Mercury in the Drainage of Wastewater
Decree on the Emission of Substances in the Drainage of Wastewater from Facilities and Plants for Plant Protection Products
Decree on Concessions for Economic Exploitation of Sea in the Piran Bay for Breeding Sea Fish Decree on the Method, Subject and Conditions for Performing Commercial Public Services of Radioactive Waste Management
Decree on the Emission of Volatile Organic Compounds into the Atmosphere from the Equipment for Storage and Decanting of Motor Fuel
Decree on the Emission of Substances in the Drainage of Wastewater from Chlorine-alkaline Electrolysis Decree on the Emission of Substances in the Drainage of Wastewater from Facilities and Plants: for the production of glass and glass products, from domestic animal breeding facilities; from stations for supplying motor vehicles with fuels; from maintenance and repair of motor vehicles facilities and car washes; from the production of plant and animal oils and fats; from facilities for performing healthcare and veterinary activities; from carcass disposal plants; from facilities for the production, processing and conservation of meat and the production of meat products; from milk processing and production of milk products; from the production of beer and malt plants, from paper, carton and cardboard production plants; from cellulose production plants
Decree on the Tax Return Form and Content for Pollution of Atmosphere with the Emission of Carbon Dioxide for Inflammable Organic Substances
Decree on Setting Up Standards for Forest Works
Decision Determining the Amount of Tax per Unit of Water Pollution for 2000
Instructions for the Formation of Prices for Compulsory Local Public Services for Drainage and
Treatment of Municipal Wastewater and Precipitation Water
Decree on Concession for Management of the Škocjan Cave Nature Reserve
Ordinance on Protection and Development of the Škocjan Cave Nature Reserve
Chemicals Act
Regulations on Special Conditions for Trade in Toxic Chemicals
Regulations on Communicating Data on Chemicals
Rules on the Classification, Packaging and labeling of Toxic Substances
Decision on Restricting Trade in Toxic Preparations for General Use Containing Monoethyleneglycol
Decision on Restricting Trade in Toxic Products for General Use Containing Naphthalene
Decision on Prohibition of Trade in and use of Toxic Substances and Products Made Thereof used as
Plant Protection Products
Chemical Weapons Act
Transport of Toxic Goods Act

## 2000

Decree on Temporary Protection of Fossil Vertebrates near Kozina
Decree on Temporary Protection of the Mlak Area
Decree on the Emission of Substances in the Drainage of Wastewater from Facilities and Plants for Coal Extraction and Production of Briquettes and Coke
Decree on the Emission of Substances into the Atmosphere from Toxic Waste Incinerators
Decree on the Emission of Substances into the Atmosphere from Municipal Waste Incinerators
Decree on the Emission of Substances in the Drainage of Wastewater from Facilities and Plants for Water Preparation
Decree on the Emission of Substances in the Drainage of Wastewater from Cooling Plants and Steam and Hot Water Production Plants

Decree on the Emission of Substances in the Drainage of Wastewater from Facilities and Plants for
Smoke Gases Treatment
Decree on the Emission of Substances in the Drainage of Leach Waters from Landfills
Decree on the Emission of Substances in the Drainage of Wastewater from Alcohol Beverages and Alcohol Production Facilities
Decree on the Emission of Substances in the Drainage of Wastewater from Facilities and Plants for Production of Mineral Water and Soft Drinks
Decree on the Emission of Substances in the Drainage of Wastewater from Facilities and Plants for the Production of Fish Products
Decree on the Emission of Substances in the Drainage of Wastewater from Facilities and Plants for Processing of Fruit and Vegetables and Food Production and Deep-Frozen Vegetables
Decree on the Emission of Substances in the Drainage of Wastewater from Facilities and Plants for Potato Processing
Decree on Concessions for the Commercial Exploitation of Water of the Individual Sections of the Watercourses of Artišnica, Zaplaninščica, Limovski Graben and Sušica for Breeding Salmonidae Fish Regulations for Removal of Polychlorinated Biphenyl and Polychlorinated Terpheny
Regulations on Monitoring Toxic Substances Pollution of Underground Water
Regulations on Waste Disposal
Instructions for the Formation of Prices for Compulsory Local Public Services for Drinking Water Supply Decree on the Method of Performing National Public Service in Water Management Instruction for Registration in the List of Legal and Natural Persons Carrying Out Production and/or Trade in Toxic Chemicals Kept by the Chemicals Office of the Republic of Slovenia Rules for Annual Reports on Performed Supervisions of Toxic Goods Transport


## 3. SURVEY OF CHANGES IN THE ENVIRONMENT SITUATION OVER NINE YEARS

A survey by individual parameter and change in the environment is specified only for the areas with available data. Data involving changes in the atmosphere have been processed to the highest extent, here, however, only data on water and some data on changes in the soil are specified.

## Quality of Water

Until 1980, the quality of ground water was acceptable. Between 1986 and 1990, the researchers performing the analyses of water sources began to warn that certain underground sources were contaminated, which started systematic research and measurements within the Special Programme of Ground Water Measurements funded by the Republic of Slovenia. The underground areas in Sorško Polje, Ljubljansko Polje, Dravsko Polje, and Mursko Polje have been systematically analysed.

The following has been established for the period between 1986 and 1990:

- Ground water in Sorško Polje was heavily polluted with pesticides, nitrites, phenol compounds, mineral oils, mercury, ammonium, organic solvents, and chlorinated phosphor compounds.
- Ground water in Ljubljansko Polje showed the presence of phenol compounds, trichloroethylene, triand hexavalent chrome and mineral oils.
- Ground water of Dravsko Polje contained pesticides.
- Ground water of Mursko Polje showed only few exceeded values of pesticide content; the water was mostly acceptable.

After 1990, analyses expanded to other fields so that systematic analyses of ground water were performed all over Slovenia. Monitoring consisted of the sampling and analysis of water in 84 places in 18 ground water fields.

A comparison between the analyses performed in 1990 and in 1995 in the same fields has demonstrated the following changes:

- Ground water in Sorško Polje was polluted with phenol compounds, chlorinated solvents and polychlorinated biphenyls.
- Ground water in Ljubljansko Polje was polluted with pesticides, chrome and organic solvents.
- Ground water of Dravsko Polje contained excessive concentrations of nitrates, pesticides, zinc, and chlorinated solvents.
- Ground water of Mursko Polje contained nitrites, pesticides and in some places halogenated solvents.

The latest data show the following results on nitrate and pesticide content in ground water in individual fields:
Table 1: Nitrate Content in Ground Water in Slovenia, 1992, 1994, 1995 and 1996

| Ground Water | Number Of Sampling Places | Samples Exceeding $50 \mathrm{Mg} / \mathrm{l}$ (\%) Content |  |  |  | Maximum Content (mg/l) |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | 1992 | 1994 | 1995 | 1996 | 1992 | 1994 | 1995 | 1996 |
| Prekmursko-Apaško Polje | 7 | 43 | 64 | 64 | 43 | 127.1 | 169.6 | 100.1 | 131.1 |
| Mursko Polje | 3 | 33 | 40 | 0 | 33 | 109.8 | 66.0 | 35.0 | 86.8 |
| Dravsko Polje - Vrbanski plateau | 10 | 59 | 55 | 59 | 64 | 86.4 | 90.8 | 83.3 | 93.0 |
| Ptujsko Polje | 4 | 50 | 33 | 50 | 50 | 104.1 | 55.8 | 115.1 | 85.9 |
| Lower Savijna Valley, Bolska, and Hudijna Valley | 11 | 82 | 76 | 60 | 67 | 130.6 | 97.4 | 112.9 | 98.3 |
| Kranjsko Polje | 4 | 0 | 0 | 0 | 0 | 30.6 | 26.6 | 30.1 | 24.8 |
| Sorško Polje | 9 | 17 | 11 | 17 | 28 | 73.5 | 58.5 | 68.2 | 75.3 |
| Kamniška Bistrica Valley, Vodiško Polje | 7 | 0 | 0 | 0 | 0 | 44.3 | 46.5 | 39.9 | 37.2 |
| Ljubljansko Polje and Barje | 11 | 0 | 0 | 0 | 0 | 27.5 | 25.7 | 27.9 | 28.3 |
| Brežiško - Čateško Polje | 5 | 0 | 0 | 0 | 0 | 11.1 | 35.4 | 25.4 | 25.2 |
| Krško Polje | 8 | 7 | 47 | 40 | 17 | 57.1 | 60.7 | 64.2 | 63.1 |
| Vipava and Soča Valley | 4 | 50 | 38 | 25 | 13 | 81.9 | 106.7 | 68.0 | 54.9 |
| Slovenia | 83 | 34 | 33 | 30 | 29 |  |  |  |  |

Table 2: Pesticide Content in Ground Water in Slovenia, 1992, 1994, 1995 and 1996

| Ground Water | Number of Sampling Places | Samples Under the Limit Value (\%)* |  |  |  | Samples Over The Limit Value (\%) |  |  |  | Maximum value ( $\mu \mathrm{g} / \mathrm{l}$ ) |  |  |  | Maximum Value** <br> ( $\mu \mathrm{g} / \mathrm{l}$ ) |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | ‘92 | '94 | '95 | '96 | '92 | '94 | '95 | '96 | '92 | '94 | '95 | '96 | '92 | '94 | '95 | '96 |
| Prekmursko-Apaško Polje | 7 | 29 | 29 | 28 | 35 | 71 | 71 | 72 | 65 | 3.83 | 2.16 | 1.83 | 1.55 | $\begin{aligned} & \hline 1.3 \\ & 0 \end{aligned}$ | 0.08 | 0.85 | 0.58 |
| Mursko Polje | 3 | 67 | 82 | 100 | 100 | 33 | 17 | 0 | 0 | 0.55 | 0.59 | 0.34 | 0.26 | $\begin{array}{\|l\|} \hline 0.2 \\ 0 \\ \hline \end{array}$ | 0.25 | 0.12 | 0.08 |
| Dravsko Polje - Vrbanski plato | 10 | 18 | 45 | 41 | 36 | 82 | 55 | 59 | 64 | 5.06 | $\begin{array}{r} 19.9 \\ 5 \\ \hline \end{array}$ | 4.41 | 3.20 | $\begin{aligned} & \hline 2.1 \\ & 0 \end{aligned}$ | 7.30 | 1.30 | 1.64 |
| Ptujsko Polje | 4 | 25 | 63 | 25 | 37 | 75 | 37 | 75 | 63 | 2.17 | 1.44 | 2.34 | 2.17 | $\begin{aligned} & 1.1 \\ & 0 \end{aligned}$ | 0.49 | 0.82 | 0.66 |
| Lower Savijna Valley, Bolska and Hudijna Valley | 11 | 36 | 57 | 65 | 71 | 64 | 43 | 35 | 29 | 1.80 | 0.95 | 0.63 | 0.74 | $\begin{aligned} & \hline 0.7 \\ & 7 \\ & \hline \end{aligned}$ | 0.23 | 0.52 | 0.74 |
| Kranjsko Polje | 4 | 71 | 100 | 100 | 100 | 29 | 0 | 0 | 0 | 0.73 | 0.27 | 0.14 | 0.31 | $\begin{aligned} & \hline 0.4 \\ & 0 \end{aligned}$ | 0.15 | 0.13 | 0.20 |
| Sorško Polje | 9 | 89 | 94 | 94 | 100 | 11 | 6 | 6 | 0 | 2.18 | 0.55 | 0.82 | 0.30 | $\begin{aligned} & 1.5 \\ & 0 \end{aligned}$ | 0.25 | 0.21 | 0.16 |
| Kamniška Bistrica Valley, Vodiško Polje | 7 | 53 | 50 | 50 | 57 | 42 | 50 | 50 | 43 | 4.66 | 3.17 | 2.70 | 1.69 | $\begin{aligned} & 0.8 \\ & 2 \end{aligned}$ | 0.56 | 0.47 | 0.34 |
| Ljubljansko Polje and Barje | 11 | 100 | 95 | 100 | 100 | 0 | 5 | 0 | 0 | 0.27 | 0.61 | 0.33 | 0.45 | - | 0.57 | 0.32 | 0.40 |
| Brežiško - Čateško Polje | 5 | 100 | 100 | 90 | 100 | 0 | 0 | 10 | 0 | 0.40 | 0.35 | 0.52 | 0 | $\begin{aligned} & 0.2 \\ & 0 \end{aligned}$ | 0.10 | 0.24 | 0 |
| Krško Polje | 8 | 93 | 69 | 81 | 100 | 7 | 31 | 19 | 0 | 0.50 | 1.04 | 0.81 | 0.48 | $\begin{aligned} & 0.3 \\ & 0 \end{aligned}$ | 0.19 | 0.13 | 0.24 |
| Vipava and Soča Valley | 4 | 100 | 100 | 100 | 100 | 0 | 0 | 0 | 0 | 0.29 | 0.05 | 0.05 | 0.05 | $\begin{aligned} & 0.2 \\ & 0 \end{aligned}$ | 0 | 0 | 0 |
| Slovenia | 83 | 63 | 68 | 70 | 77 | 37 | 32 | 30 | 23 |  |  |  |  |  |  |  |  |
| Legend: <br> * Limit value for pesticide sum is $0.5 \mu \mathrm{~g} / \mathrm{l}$ <br> ** Limit value for atrasine is $0.1 \mu \mathrm{~g} / \mathrm{l}$ <br> Data source: MEPP, HI |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |

## Quality of the Soil

Pollution of the soil is the consequence of contaminants accumulating in the soil over a longer period. Sources of such pollution are usually individual producers of these substances, which means that they could be classified as point sources or strictly local sources. It has been established that in Slovenia the pollution of the soil involves mainly unsuitable management of special waste, emissions of contaminants into the atmosphere, composting waste substances, incorrect disposal of sediments and mud from municipal and other treatment plants, inappropriate management of agricultural waste, inappropriate use of pesticides, etc.

Measurements of the soil began before 1990, but only in certain areas where the environment was heavily polluted by industry and emissions into the atmosphere and water, and an increased number of certain diseases was established. This was the reason for the analyses. The region around the town of Celje was researched the most. The results of the measurements, which had taken place in 1989, showed that the concentrations of selenium, mercury, titanium, copper, and chromium did not exceed the standards in force in the European Community at that time. The DDT, DDE, and TDD values were increased, but only in individual locations. The concentrations of cadmium, lead, zinc, arsenic, nickel, and certain fluorides, however, were exceeded. Table 3 demonstrates the measured values.

Table 3: Content of Certain Metals in Soil Samples in the Area of Celje Municipality

| Metal | Content of the Element in the <br> Celje Region <br> $(\mu \mathbf{g} / \mathbf{g}$ of dry substance) | EGS and Alps Adriatic <br> Countries Standards <br> $(\mu \mathbf{g} / \mathbf{g}$ of dry substance) |
| :--- | :---: | :---: |
| Copper | $5.6-100$ | 100 |
| Zinc | $55-3010$ | 300 |
| Lead | $15-810$ | 100 |
| Chromium | $4.8-61.1$ | 100 |
| Cadmium | $0.1-21.4$ | 2 |
| Nickel | $1.9-76$ | 60 |
| Arsenic | $<1-85$ | 20 |

Source: Bio-technical faculty of the University in Ljubljana 1989
Note: All samples were taken in 1989

After 1990, the research of the soil began to be performed more intensively, with various institutions, such as faculties, research institutes, etc. introducing a type of research studies involving the monitoring of the soil with respect to different contaminants. Via its official institutions, such as the Ministry of the Environment, the state started to become involved in this monitoring much later and much less intensively than expected and was necessary. Therefore, the data that are the result of these analyses have been obtained from the University and different doctorate theses that consisted of analysing and measuring the environmental pollution parameters.

At the beginning of 1990, the monitoring of the soil encompassed mainly farmland and forests, on the basis of the Decree on Establishing Pollution of Farmland and Forest (Ur.l. RS, no. 6/1990) and later pursuant to Regulations on Normatives, Analytic Procedures and Methods of Establishing Pollution of the Soil and Vegetation, and Conditions for the Use of Certain Substances in Agriculture and Forestry (Ur.l. RS, no. 7/1990).

The parameters, such as cadmium, zinc, and lead content have been measured in the same area (the Celje region) as in 1989. At the same time, systematic measurements of the soil in different regions have begun, as shown in the Table 4.

Table 4: Regional Soil Measurements

| Place | Year | Number of <br> Samples | Number of <br> Samples of Soil | Number of <br> Samples of Plants |
| :--- | :---: | :---: | :---: | :---: |
| Celje | 1989 | 126 | 378 | 40 |
| Ljubljana | 1991 | 5 | 11 | 0 |
| Ljubljana | 1991 | 26 | 70 | 22 |
| Jesenice | 1991 | 11 | 28 | 10 |
| Krško polje | 1991 | 15 | 45 | 12 |
| Ptujsko polje | 1991 | 21 | 63 | 18 |
| Koprsko | 1991 | 16 | 48 | 16 |
| Ljutomer | 1991 | 1 | 3 | 5 |
| Celje | 1993 | 5 | 15 | 5 |
| Domžale | 1994 | 3 | 9 | $* 0$ |
| Novo mesto | 1994 | 21 | 59 | 21 |
| Anhovo | 1995 | 4 | 9 | 4 |
|  | TOTAL | $\mathbf{2 5 4}$ | $\mathbf{7 3 8}$ | $\mathbf{1 5 3}$ |

After 1995 the Ministry of the Environment and Physical Planning adopted, pursuant to the Environment Act, a number of decrees with the view of regulating the protection of the soil by law:

- Decree on the Limit, Warning and Critical Emission Values of Toxic Substances in Soil
- Decree on Input of Toxic Substances and Plant Nutrients into the Soil
- Regulations on Operational Monitoring in Input of Toxic Substances and Plant Nutrients into the Soil

These regulations set up limit and critical emission values for a number of contaminants and their input into the soil. These values have been taken over from foreign legislation.

Systematic monitoring of the content of certain contaminants in the soil has shown that Slovenia has some areas that are heavily polluted. In the most polluted areas, it has been established that in the regions with intensive agriculture the main contaminants were pesticides, in the vine-growing regions the main contaminant was copper, in the regions with excessive use of fertilisers, ground water was polluted with nitrates, and in the areas where industrial waste had been inappropriately disposed the main contaminants were heavy metals and aromatic hydrocarbons. The lead content near the main motorways was also high.

## 4. AN OVERVIEW OF CONDITIONS IN THE AREA OF WASTE MANAGEMENT AND DISPOSAL

## Waste

Waste management in Slovenia is still not institutionally regulated on a state level. Despite many documents prepared on the subject, practical measures have not yet been undertaken.

The situation in 1990 was as follows: Sixty-five percent of the population was included in the public municipal waste disposal system. In 1987, 320,000 tonnes of municipal waste were created in Slovenia,
or $1,800,000 \mathrm{~m}^{3}$. Between 1981 and 1987, the quantity of municipal waste increased by a minimum of $5 \%$ and by a maximum of $10 \%$ in major cities (Table 5).

Table 5: Quantity of Municipal Wastes Produced in Regions of Slovenia in 1981 and 1987

| Region | 1981 |  | 1987 |  | Index (87/81) |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | Quantity of wastes (tons) | Number of Inhabitants | Quantity of Wastes (tons) | Number of Inhabitants |  |
| Pomurska | 20871 | 130442 | 21111 | 131946 | 101,1 |
| Podravska | 51234 | 320215 | 52532 | 328425 | 102,5 |
| Savinjska | 39013 | 243834 | 40998 | 256240 | 105,1 |
| Koroska | 11191 | 69945 | 11767 | 73546 | 105,1 |
| Zasavska | 7409 | 46304 | 7595 | 47470 | 102,5 |
| Posavska | 11589 | 72432 | 11642 | 72764 | 100,5 |
| Ljubljanska | 75221 | 470130 | 82752 | 517202 | 110,0 |
| Dolenjska | 15724 | 98276 | 16344 | 102153 | 103,9 |
| Notranjska | 7934 | 49589 | 8060 | 50372 | 101,6 |
| Obalno-kraska | 14900 | 93127 | 15896 | 99349 | 106,7 |
| Goriska | 18931 | 118320 | 19252 | 120322 | 101,6 |
| Gorenjska | 28680 | 179250 | 30364 | 189773 | 105,9 |
| TOTAL | 302697 | 1891864 | 318313 | 1989462 | 105,2 |

Table 6: The Composition of Municipal Waste

| Material | Part (\%) | Quantity of Wastes <br> Produced in 1 Year | Quantity of Wastes <br> Collected in 1 Year |
| :--- | ---: | ---: | ---: |
| Paper | 15 | 45000 | 30150 |
| Plastics | 10 | 30000 | 20100 |
| Glass | 5 | 15000 | 10050 |
| Metals | 7 | 21000 | 14070 |
| Textile | 4 | 12000 | 8040 |
| Organic compounds | 41 | 123000 | 82410 |
| Inorganic compounds | 18 | 54000 | 36180 |
|  | $\mathbf{1 0 0}$ | $\mathbf{3 0 0 0 0 0}$ | $\mathbf{2 0 1 0 0 0}$ |

In 1995, around 900,000 tonnes of municipal waste were created in Slovenia, which represented $10 \%$ of all wastes created in Slovenia in that year. In that same year, the percentage of the population included in the public municipal waste disposal system reached $76 \%$. The composition of municipal waste in 1995 was similar to that in 1987. Approximately 100,000 tonnes of waste were separated and recycled, while 750,000 tonnes were disposed of in landfills only.

The conditions in the area of special types of waste management have changed greatly over the past few years, in terms of structure as well as quantity. This is attributed to the changes in the political and economic systems and to the concern for the environment connected to this, as well as to cost-cutting in production, the closing of industrial plants in various unprofitable branches, and so on. Table 7 shows the quantities of special types of waste created in 1987.

Table 7: Quantities of Special Types of Waste Generated in 1987

| Category | Type of Waste | Quantity |  |  |  |  |  |  |
| :--- | :--- | ---: | ---: | :---: | :---: | :---: | :---: | :---: |
|  |  | (tons) | $\left(\mathbf{m}^{\mathbf{3}}\right)$ |  |  |  |  |  |
| I. | Particularly hazardous wastes | 447 | 4.293 |  |  |  |  |  |
| II. | Hazardous wastes | 24.118 | 385.573 |  |  |  |  |  |
| III. | Special wastes | 740.384 | 1.160 .872 |  |  |  |  |  |
|  |  |  |  |  |  |  | $\mathbf{7 6 4 . 9 4 9}$ | $\mathbf{1 . 5 5 0 . 7 3 8}$ |

In practice, the management of special types of waste was completely unregulated on the state level. Such waste was mostly disposed of in mono landfills, in municipal waste landfills and in various "illegal" landfills. Secondary raw materials were only rarely recycled from such waste. Table $\mathbf{8}$ shows the recycled quantities of secondary raw materials from 1985 to 1988.

Table 8: Recycled Quantities of Secondary Raw Materials from 1985 to 1988

|  | Quantity (tons) |  |  |  | Structure 1988 (\%) | $\begin{aligned} & \text { Index } \\ & \text { 1988/86 } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Raw Material | 1985 | 1986 | 1987 | 1988 |  |  |
| Steel and castings | 272728 | 259660 | 293395 | 367291 | 75,1 | 141 |
| Heavy metals | 16215 | - | - | - |  |  |
| Copper and alloys | - | 7063 | 7663 | 6222 | 1,3 | 88 |
| Aluminium and alloys | - | 6323 | 6932 | 5709 | 1,2 | 90 |
| Lead and alloys | - | 3042 | 2688 | 2974 | 0,6 | 98 |
| Zinc and alloys | - | 380 | 358 | 340 | 0,1 | 89 |
| Paper | 84210 | 89197 | 80613 | 80027 | 16,4 | 90 |
| Plastics | 2715 | 2312 | 2212 | 1715 | 0,4 | 74 |
| Glass | 17448 | 17516 | 17427 | 16283 | 3,3 | 93 |
| Rubber | 3248 | 3439 | 2369 | 2453 | 0,5 | 71 |
| Textiles | 4244 | 5841 | 5445 | 5234 | 1,1 | 90 |
| Others | 6549 | 945 | 753 | 780 | 0,2 | 83 |
| TOTAL | 407357 | 395718 | 419855 | 489028 | 100,0 | 124 |

Classification and measurements of special types of waste between 1993 and 1996 shows that the quantities and variety of waste changed greatly. Table 9 shows these quantities and varieties over the years, according to the definitions in legal acts passed after 1992 and still in force today.

Table 9: Quantity of Dangerous Waste Between 1993 and 1996

| Type of Waste | $\begin{gathered} \hline \mathbf{m}^{3} \\ 1993 \end{gathered}$ | $\begin{gathered} \mathrm{t} \\ 1993 \end{gathered}$ | $\begin{gathered} \hline \mathbf{m}^{3} \\ 1994 \end{gathered}$ | $\begin{gathered} \hline \mathrm{t} \\ 1994 \end{gathered}$ | $\begin{gathered} \hline \mathbf{m}^{3} \\ \mathbf{1 9 9 5} \end{gathered}$ | $\begin{gathered} \mathrm{t} \\ 1995 \end{gathered}$ | $\begin{gathered} \hline \mathbf{m}^{3} \\ 1996 \end{gathered}$ | $\begin{gathered} \hline \text { t } \\ 1996 \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Medical waste | 416 | 324 | 474 | 286 | 831 | 28 | 631 | 329 |
| Pharmaceutical production and preparation | / | 269 | 1030 | 868 | 931 | 1226 | 892 | 921 |


| Type of Waste | $\begin{gathered} \hline \mathbf{m}^{3} \\ 1993 \end{gathered}$ | $\begin{gathered} \hline t \\ 1993 \end{gathered}$ | $\begin{gathered} \hline \mathrm{m}^{3} \\ 1994 \end{gathered}$ | $\begin{gathered} \hline t \\ 1994 \end{gathered}$ | $\begin{gathered} \hline \mathbf{m}^{3} \\ \mathbf{1 9 9 5} \end{gathered}$ | $\begin{gathered} \hline \mathbf{t} \\ 1995 \end{gathered}$ | $\begin{gathered} \hline \mathbf{m}^{3} \\ 1996 \end{gathered}$ | $\begin{gathered} \hline t \\ 1996 \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Pharmaceutical products, narcotic drugs, and medicaments | 0 | 7 | 0 | 21 |  | 27 |  | 104 |
| Production, preparation and use of pesticides and plant protection products | 2 | 696 | 21 | 272 |  | 157 | 2 | 204 |
| Production, preparation and use of chemicals for wood protection |  |  |  |  |  |  |  |  |
| Production, preparation and use of organic solvents |  |  |  |  |  |  |  |  |
| Heat treatment and hardening that contains cyanides |  |  |  |  |  |  |  |  |
| Mineral oil waste, waste unsuitable for initiallydesignated use | 936 | 849 | 1084 | 913 | 1057 | 719 | 1241 | 753 |
| Waste mixtures oil/water, hydrocarbons/water, and emulsions | 4407 | 1003 | 2141 | 279 | 3724 | 703 | 3007 | 800 |
| PCB, polychlorinated triphenyls (PCT) and polybrominated biphenyls (PBB) | 2 | 72 | 0 | 17 | 2 | 28 | 4 | 14 |
| Residues of tar from refining, distillation and pyrolitic treatment |  | 36 |  | 30 |  |  |  |  |
| Production, preparation and use of inks, dyes, pigments, coats, and varnishes | 3125 | 566 | 1293 | 572 | 1123 | 410 | 1128 | 555 |
| Production, preparation and use of pitches, latex, plastic additives, glues | 258 | 512 | 123 | 172 | 101 | 142 | 226 | 184 |
| Chemicals from research and development |  |  |  |  |  |  |  |  |
| Explosive wastes not regulated by other laws | 2009 | 84 | 1166 | 4 | 3742 | 2 | 3981 | 2 |
| Production, preparation and use of photographic chemicals | 5 | 34 | 32 | 918 | 14 | 1121 | 11 | 961 |
| Superficial treatment of metals and plastic | 2 | 102 | 2 | 132 | 1 | 42 | 1 | 49 |
| Residue from removing industrial waste | 80 | 1141 | 438 | 1198 | 987 | 20 | 1163 | 19 |
| Metal carbonyls |  |  |  |  |  |  |  |  |
| Beryllium, beryllium compounds |  |  |  |  |  |  |  |  |
| Hexavalent chrome compounds | 82 | 55 | 7 | 34 | 4 | 18 | 4 |  |
| Copper compounds |  | 3 | 4 | 3 | 4 | 0 |  | 0 |
| Zinc compounds | 11 | 1064 | 2 | 885 | 1 | 1254 | 11 | 1201 |
| Arsenic, arsenic compounds | 1 |  | 0 |  | 2 |  |  |  |
| Selenium, selenium compounds |  |  |  |  |  |  |  |  |


| Type of Waste | $\begin{gathered} \hline \mathbf{m}^{3} \\ 1993 \end{gathered}$ | $\begin{gathered} \hline \mathrm{t} \\ 1993 \end{gathered}$ | $\begin{gathered} \hline \mathbf{m}^{3} \\ 1994 \end{gathered}$ | $\begin{gathered} \hline \mathrm{t} \\ 1994 \end{gathered}$ | $\begin{gathered} \hline \mathbf{m}^{3} \\ \mathbf{1 9 9 5} \end{gathered}$ | $\begin{gathered} \hline \mathrm{t} \\ 1995 \end{gathered}$ | $\begin{gathered} \hline \mathbf{m}^{3} \\ \mathbf{1 9 9 6} \end{gathered}$ | $\begin{gathered} \hline \mathrm{t} \\ 1996 \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Cadmium, cadmium compounds |  |  |  |  |  |  |  |  |
| Antimony, antimony compounds |  |  |  |  |  |  |  |  |
| Tellurium, tellurium compounds |  |  |  |  |  |  |  |  |
| Mercury, mercury compounds |  | 7558 |  |  |  | 0 |  | 0 |
| Thallium, thallium compounds |  |  |  |  |  |  |  |  |
| Lead, lead compounds | 1 | 17 |  | 45 | 0 | 50 |  | 428 |
| Inorganic fluorine compounds without calcium fluoride |  |  |  |  |  |  |  |  |
| Inorganic cyanides | 9 | 162 | 8 | 158 | 0 | 202 | 0 | 133 |
| Acid solutions or solid acids | 938 | 1358 | 449 | 151 | 490 | 141 | 442 | 1727 |
| Basic solutions or solid bases | 720 | 662 | 558 | 642 | 728 | 1218 | 774 | 599 |
| Asbestos | 39 | 3417 | 839 | 6081 |  | 4775 | 1 | 4892 |
| Organic phosphor compounds |  |  |  |  |  |  |  |  |
| Organic cyanides |  |  |  |  |  |  |  |  |
| Phenol, phenol compounds including chloro-phenols | 744 | 616 |  | 13 | 220 | 603 | 158 | 588 |
| Ethers |  | 2 |  | 1 |  | 0 |  | 0 |
| Halogenated organic solvents | 522 | 238 | 179 | 186 | 71 | 159 | 44 | 205 |
| Organic solvents without halogenated solvents | 1289 | 2050 | 543 | 2405 | 347 | 3840 | 200 | 4496 |
| All ingredients related to polychlorinated dibenzofuran |  |  |  |  |  |  |  |  |
| All ingredients related to polychlorinated dibenzo-pdioxin |  |  |  |  |  |  |  |  |
| Organo-halogenated compounds not specified under $\mathrm{Y} 39, \mathrm{Y} 41, \mathrm{Y} 42, \mathrm{Y} 43, \mathrm{Y} 44$ | 3 | 0 | 1 | 3 | 0 | 2 | 1 |  |
| Waste from households |  |  |  |  | 807 | 56 | 0 | 56 |
| Waste from incinerating household waste |  |  |  |  |  |  |  |  |
| Sum | 15601 | 22897 | 10394 | 16289 | 15187 | 16943 | 13922 | 19221 |

Management of such wastes has not changed greatly since 1987, which means that in the majority of cases it is still collected and disposed of in more or less unregulated landfills. The separation and recycling of raw materials from waste is in decline compared to the period between 1985 and 1988 (Table 8); therefore, raw material potential is being wasted due to a lack of appropriate economic measures. Even though certain well-developed recycling procedures for specific types of special waste in certain branches have been in use for a number of years, a large quantity of such waste is still disposed of in landfills, completely unutilised.

In terms of energy, the caloric value of waste is harnessed in two incinerators for special types of industrial waste, specifically for pharmaceutical waste (capacity 700 tonnes/year) and phytopharmaceutical waste (capacity 100 tonnes/year).

## Landfills

The most problematic activity in waste management is disposal in landfills. A comparison of the number and fittings of landfills in Slovenia shows that waste treatment has not significantly changed. A total of 54 official municipal waste landfills were located in Slovenia before 1990 (see Figure 2).

Figure 2: Official municipal waste landfills in Slovenia


All of the described landfills operate without fulfilling the required technical and geological demands, and only 16 of them have legal operational permits. Between 1991 and 1994, 18 landfills were reconstructed, but advanced technical solutions, such as treatment of water leakage, elimination of gases, monitoring, disposal techniques, and so on, were used in only four. In addition to these landfills, approximately 600 "black" or illegal landfills for all types of waste are thought to exist. Their locations are known, but they operate without operational permits and are not officially registered.

Apart from the above, several years ago various non-governmental organisations began to search for, register and mark various pits where industries were disposing of their waste, and also registered waste illegally disposed of, which had been mostly covered with earth. Such landfills were mostly discovered due to toxic substances leaking into ground water, and often quite accidentally during construction works or the like. The number of these sites exceeds 10,000 .

Figure 3: Registered Caves in the Land Register of Slovenian Caves


Figure 4: Polluted or Damaged Caves in the Same Land Register


There are also 13 landfills in Slovenia for industrial waste and waste from prospecting of mineral resources (see Figure 5).

Figure 5: Locations of 13 Industrial Waste and Mining Landfills


The capacity of all registered official municipal waste landfills (54 in number) is approximately $13,000,000 \mathrm{~m}^{3}$. Waste is compressed prior to disposal in these landfills to reduce its size. These landfills are also the end destination of waste discovered in illegal landfills; their capacities are projected to suffice only for the next five to seven years. Figure 6 shows the disposal of waste in registered official municipal waste landfills.

The consequences of water leakage from illegal landfills already surfaced several years ago as water contamination in certain areas. This was most evident in the northeastern part of the country where drinking water had to be supplied by tankers to more than 60,000 people.

## 5. National Programme for the Protection of the Environment

The most important document drawn up by the Ministry of the Environment and Physical Planning in the last ten years is, in addition to the Environmental Protection Act, the National Programme for the Protection of the Environment. It contains goals, guidelines and the strategy for the protection of the environment for the period of a minimum of ten years.

The document was published in official documents in September 1999 but it has not yet been adopted by the National Assembly. With the National Assembly not adopting and confirming the legitimacy of the document, all guidelines and plans defined in the document have not yet become operational.

The document consists of sets of basic goals, which are placed in the document with respect to meaning and time plan of the implementation.

Figure 6: Disposal of Wastes in Registered Official Municipal Waste Landfills


These goals are:

## Water

- reducing emissions from point sources
- reducing emissions from diffusing sources
- clear-up of old pollution posing a threat to the aquatic environment
- clear-up and prevention of unsuitable encroachments into the aquatic environment


## Waste management

- reducing the generation and risk potential of waste at the source
- increasing the exploitation of waste in terms of substance and energy, and reducing the emission of greenhouse gases
- establishing an effective system of waste management
- gradual elimination of old pollution


## Biotic diversity and genetic sources

- preventing the reduction of biotic diversity at the ecosystem level
- preventing further threats to the natural balance due to inappropriate exploitation of plant and animal species


## Atmosphere

- reducing the pollution of the atmosphere by industrial sources
- reducing the emissions from coal-fired power plants
- controlling pollution of the atmosphere due to traffic
- reducing emissions from individual and joint combustion chambers in residential areas
- reducing the causes for photochemical smog and troposphere ozone
- elimination of CFC use
- reducing the emissions of greenhouse gases
- controlling the problems of long-distance atmosphere pollution


## Soil and Forest

- limiting chemical soil pollution and implementation of urgent cleanups
- limiting physical degradation of soil
- limiting further degradation of forest soil


## Noise

- reducing road-traffic-induced noise
- reducing noise from other sources


## Ionic radiation

- providing for effective management of radioactive waste
- controlling radioactive radiation in the external environment


## Non-ionic radiation

- identifying and gradually controlling individual sources of non-ionic radiation


## Risks

- providing for suitable procedures for handling chemicals and genetically altered organisms in their production, traffic and use
- establishing appropriate storage, transport and disposal of chemicals.

According to this document Slovenia's priority goals for the first five years of this millennium are the following:

- effective completion of the set programmes for the protection of the atmosphere supplemented by the programmes for reducing industrial concentrations of troposphere ozone and emissions of greenhouse gases
- improving the situation in the aquatic environment
- establishing modern methods of waste management
- preserving and protecting biotic diversity and genetic sources.

The concept of the National Programme for the Protection of the Environment takes into consideration the principles of the effectiveness of every sector or activity, which affect the environment, and does not release any activity of its responsibility toward the environment. The document defines programmes for individual industrial activities that affect the degradation of the environment by industry and mining, power industry, agriculture and forestry, and tourism.

At the same time the document deals with specific environmental problems of sensitive areas the coast, countryside, and mountainous areas. A question that comes to mind is whether the national programme will receive its verification in the National Assembly and its implementation in practice.

## 6. FINANCIAL PROBLEMS

Slovenia's state administration, and the Ministry of the Environment and Physical Planning in particular, are well aware that environmental care and rehabilitation and the organisation of activities for keeping pollution-causing parameters within reasonable and legal boundaries are extremely costly and demanding processes. In formulating the Strategic Orientation on Waste Management, the legislature envisaged economic measures that would be necessary in order to enable these activities to commence and function.

Table 10 shows that the proponents of the Strategic Orientation on Waste Management in the Republic of Slovenia have envisaged activities in connection with landfills, application of technical and technological measures and introduction of heat processing of waste, and also in connection with the management of
industrial, agricultural and forestry waste. They have also determined the amounts to be invested in individual stages of each of these activities.

Table 10: Catalogue of the Main Activities and Investments

| Number Of Activities Related To Deposit Sites |  |  |  |
| :--- | :--- | :---: | :---: |
| 1.Land filling deposit sites by 2000, closing down and covering <br> over according to EU standards | 16 | Investment (in <br> DEM million) |  |
| 2.Land filling by 2000, and closing down according to EU <br> standards | 2 | 11 |  |
| 3.Land filling by 2000, reconstruction according to EU standards | 2 | 5 |  |
| 4.Possibility of exploitation by 2000 along the reconstruction <br> according to EU standards | 10 | 54 |  |
| 5.Reconstruction according to EU standards because of the <br> possibility of exploitation of the capacities after 2000 | 11 | 77 |  |
| 6.Expansion and reconstruction according to EU standards for <br> bridging transitional period | 8 | 145 |  |
| 7.Reconstruction and additional construction of deposit sites with <br> long-term perspective according to EU standards | 2 | 103 |  |
| 8.Construction of new deposit sites in accordance with EU <br> standards | 3 | 210 |  |
| 9. Preliminary works for new deposit site | 1 | 5 |  |

$\left.\begin{array}{|l|l|r|}\hline \text { No. } & \begin{array}{l}\text { Activities for the Implementation of Technical/Technological Complex: } \\ \text { Capture, Treatment, Processing, Exploitation of Substance }\end{array} & \begin{array}{l}\text { Investment (in } \\ \text { DEM million }\end{array} \\ \hline 1 . & \begin{array}{l}\text { Collection systems for, } \\ -\quad \text { biological, green waste } \\ \text { other waste } \\ \text { dangerous waste in household waste } \\ \text { Recycling collectors: paper, } \\ \text { glass (white, coloured) } \\ \text { metal (cans) } \\ \text { artificial mass (selected) }\end{array} & 17 \\ \hline 2 . & \begin{array}{l}\text { Collection and conversion centres for potential secondary raw materials }\end{array} & 25 \\ \hline 3 . & \begin{array}{l}\text { Compost places: } \\ -\quad 4 \text { major ones: Ljubljana, Maribor, Celje, Kranj (20,000 tonnes/yr or more) }\end{array} & \\ \hline 4 . & -\quad 40 \text { small ones (up to 6,000 tonnes per year) }\end{array}\right)$

| No. | Activity for the implementation of heat treatment of waste, and realisation <br> and construction of suitable deposit sites | Investment <br> (in DEM <br> million) |
| :--- | :--- | ---: |
| 1. | Preliminary works for two plants | 30 |
| 2. | Preliminary works and construction of one plant | 220 |
| 3. | Construction of the second plant for heat treatment of waste (after 2000) | 300 |


| No. | Activities for Realisation of Solutions in the Area of Waste from Industry, <br> Power Industry, and Construction | Investment <br> (in DEM <br> million) |
| :--- | :--- | ---: |
| 1. | All investment from long-term reservations within the ownership <br> transformation, and the exploitation of up to 30 percent of slag and ashes from <br> coal-fired plants and metallurgy in construction | 230 |
| 2. | Stationary systems for re-cycling construction waste (five plants), mobile <br> recycling devices (two devices), portable sowing devices (two), five mono <br> deposit sites, investment into plants for exploitation of energy and metallurgy <br> slag in construction | 192 |
| 3. | Funds for technological upgrading, production for reducing quantities of waste | 200 |


| No. | Activities for the Implementation of Solutions in the Area of Waste from <br> Agriculture and Forestry | Investment <br> (in DEM <br> million) |
| :--- | :--- | ---: |
| 1. | Change of technologies for breeding cattle in farms (five farms), technical and <br> technological measures for reducing the amount of slurry, measures for <br> optimisation of possibilities for use of liquid manure and slurry in agricultural <br> areas | 50 |
| 2. | Upgrading the equipment of carcass disposal plant | 25 |
| 3. | Construction of compost places (or co-investment) | 15 |
| 4. | Construction of plants substantial exploitation of wood bio-mass | 0,1 |

Investment estimate is -20 to +30 percent.
The state has also planned certain economic measures for the implementation of other environmental protection directives. One of the most important was the founding of Ekosklad (Ecofund), which may only finance environmental projects. The fund was made possible by the Environmental Protection Act. Ekosklad is a non-profit organisation, fully owned by the state, which functions as a joint-stock company. Ekosklad grants loans from its own assets at an interest rate lower than that of commercial rates. The fund does not grant non-returnable loans. All loans are intended exclusively for the financing of projects of environmental rehabilitation, improvement or conservation (such as technologies for lower energy consumption in the * industry, construction industry, etc.).

Table 11: Budgetary Spending on the Environment between 1994 and 1996 (in SIT million)

|  | 1994 <br> Value | 1994 <br> Share | 1995 <br> Value | 1995 <br> Share | 1996 <br> Value | 1996 <br> Share |
| :--- | ---: | ---: | ---: | ---: | ---: | ---: |
| Total expenditures | 4,565 | $100 \%$ | 4,107 | $100 \%$ | 3,913 | $100 \%$ |
| Investment expenditures | 3,074 | $67 \%$ | 3,085 | $75 \%$ | 1,834 | $47 \%$ |
| Current expenditures | 1,491 | $33 \%$ | 1,021 | $25 \%$ | 2,079 | $53 \%$ |
| Transfer into companies | 1,191 | $26 \%$ | 406 | $10 \%$ | 1,092 | $28 \%$ |

Note: Data may be changed since the methodology is being drawn up.
Source: The state budget

Expenditures are exclusively for environmental purposes or for items with evidently favourable effects on the environment (e.g., expenditures for improving energy efficiency). The difference between the protection of the environment and the protection of nature has not yet been determined. Estimates do not include non-returnable funds in the form of past income from tax deductions, relief, exemptions, loans or other forms of fiscal incentives for environmental expenditures. State guarantees for environmental projects are not included either.

Table 12: Ekosklad's Performance in 1994, 1995, and 1996

|  | Income Statement (in SIT million) |  |  |
| :--- | :--- | :--- | :--- |
|  | $\mathbf{1 9 9 6}$ | $\mathbf{1 9 9 5}$ | $\mathbf{1 9 9 4}$ |
| Interest | 110.2 | 44.4 | 21.6 |
| Income form securities | 90.7 | 20.7 | - |
| Net charges and commissions | $(1.3)$ | $(1.4)$ | $(0.1)$ |
| Other operating income | 7.5 | 2.0 | - |
| General administrative expenditures | $(129.7)$ | $(69.5)$ | $(18.7)$ |
| Depreciation | $(12.1)$ | $(9.6)$ | $(0.4)$ |
| Other operating expenditures | $(198.7)$ | $(8.6)$ | $(2.3)$ |
| Write-offs and adjustment | $(31.6)$ | $(11.5)$ | - |
| Of non-repaid loans | $(128.4)$ | $(104.0)$ | - |
| Income from revoked commissions | $(37.3)$ | 70.5 | 0.1 |
| Operating profit or loss | 39.9 | $(5.4)$ | - |
| Extraordinary profit or loss | 2.5 | 65.1 | 0.1 |
|  |  |  |  |

Eco Fund is a joint stock company. It is presently owned by the state. By statute, any legal entity and/or natural person may become Eco Fund shareholder. The Fund is a non-profit organisation and does not give dividends. If, in addition to the state, the owners of the Fund shares are also other shareholders, they may benefit only from preference loans. A new shareholder may not own more than $33 \%$ of Eco Fund's capital stock. Shareholders have no right to vote. The Fund is managed by the board-appointed by the government (chair and four members).

The Director of the Fund is appointed by the management board and confirmed by the government. The Fund performs its activities in four main areas: the reduction of the pollution of the atmosphere, discontinuation of ozone-harmful substances, development of municipal infrastructure and the reduction of industrial pollution. In June 1996, the Fund took up a loan at the World Bank in the amount of DEM 30 million for funding the transition to cleaner heating systems. The PHARE programme raised ECU 400,000 for institutional consolidation and projects of reducing the pollution of the atmosphere.

The Trust Fund at the Global Environmental facility has assigned USD 6.2 million of non-returnable funds to six Slovene companies for the implementation of the project of discontinuation of ozone-harmful substances. As a financial agent the Eco Fund has been dividing funds and is responsible for other procedures. In November 1995, the Eco Fund started to carry out the projects of municipal infrastructure. It published a tender for municipalities that wished to obtain loans for projects related to the sewage system, waste, systems of treating wastewater, disposal of solid waste and water system. By the spring of 1996, the loans amounted to DEM 7 million.

A similar project started in June 1996, with the tender for industrial companies that wished to obtain loans for projects related to the reduction of the pollution of the environment (atmosphere, water, solid waste and ozone-harmful substances). By November DEM 11 million loans were assigned (Table 13).

Table 13: Balance Sheet (in SIT million) for 31 December

|  | $\mathbf{1 9 9 6}$ | $\mathbf{1 9 9 5}$ | $\mathbf{1 9 9 4}$ |
| :--- | :--- | :--- | :--- |
| Cash | 42.5 | 42.6 | 25.6 |
| Loans to banks | 710.7 | 825.8 | 131.6 |
| Loans to clients | $4,313.7$ | $3,251.8$ | $2,244.0$ |
| Securities on the market | 676.7 | 459.8 | 84.2 |
| Tangible fixed assets | 13.5 | 16.7 | 21.5 |
| Other assets | 17.2 | 14.2 | 9.1 |
| Total assets | $6,157.3$ | $4,610.8$ | $2,515.9$ |
|  |  |  |  |
| Generated expenditures and | 6.7 | 10.3 | - |
| Deferred income <br> Other liabilities <br> Reservations |  |  |  |
| Registered capital <br> Reserves | 12.6 | 6.0 | 5.0 |
| Revaluation adjustment to capital | 5703.4 | 482.3 | 479.0 |
| Net profit carried over |  |  |  |
| from previous year | 65.3 | 3,8712 | $2,031.8$ |
| Net annual profit (loss) | - | 0.1 | 0.1 |
|  | 2.75 .7 | - |  |
| Total liabilities and ownership capital: | $6,157.3$ | 0.1 | - |

## Implementation costs of the National Programme for the Protection of the Environment

The document divides the implementation costs of the programme into individual goals. The estimate has been made for the initial five years from 1999 to 2003.

Table 14: Survey of Estimated Implementation Costs (in million SIT)

| Year | Water | Waste | Biodiversity | Atmosphere | Soil | Noise | Radiation | Risk | Measures | Total |
| :---: | :---: | :---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: | :---: |
| $\mathbf{1 9 9 9}$ | 27.122 | 17.570 | 2.095 | 6.047 | 49 | 50 | 56 | 58 | 142 | 53.189 |
| $\mathbf{2 0 0 0}$ | 27.002 | 17.520 | 2.095 | 6.021 | 49 | 11 | 40 | 58 | 94 | 52.890 |
| $\mathbf{2 0 0 1}$ | 26.974 | 17.520 | 2.071 | 5.975 | 28 | 9 | 10 | 9 | 2 | 52.598 |
| $\mathbf{2 0 0 2}$ | 26.974 | 17.520 | 2.093 | 5.945 | 28 | 9 | 10 | 5 |  | 52.584 |
| $\mathbf{2 0 0 3}$ | 26.974 | 17.520 | 1.809 | 5.895 | 28 | 8 | 12 | 5 |  | 52.251 |
| Total | 135.046 | 87.650 | 10.163 | 29.883 | 182 | 87 | 128 | 135 | 238 | 263.512 |

- The estimated costs by individual sectors and priority goals have been defined in detail. The financial plans of funding sources have also been defined:
- public sector
- the budget
- charge for the pollution of the environment (charge for polluting water with wastewater, charge for waste disposal, charge for gas emissions, etc.)
- municipal budgets
- foreign sources (international loans, etc.)
- the Eco Fund loans.


## Economic Instruments

The Environmental Protection Act provides the legal foundation for taxes and fees that the state may collect from polluters. Slovenia finances its environmental protection activities from several sources, as follows:

- the central budget (taxes and fees),
- municipal budgets (local taxes, donor contributions),
- company assets (companies in stages of privatisation reserve some of their assets for environmental issues),
- foreign sources of funding (international loans, assistance on the basis of bilateral agreements, etc.).
- types of taxes:
- tax on polluted wastewater
- fee for drinking water
- tax on excess air pollution from carbon dioxide
- funds from concessions to use natural resources


## 7. CONCLUSION

Over the nine years since Slovenia gained its independence, Slovenia's citizens have expected much more in the way of environmental protection than the state has actually provided. They expected great changes in those areas where the state can actively interfere through its regulations; for example, the founding of public companies for waste management, construction of landfills, water management, water conservation, protection of nature, forests and biodiversity, linking of economic and environmental developmental policies, introduction of cleaner, safer and more rational technologies in industry, environmental protection in the energy sector, and similar issues. What they have in fact received are a number of executive acts (and even those were issued under pressure from the EU, which Slovenia would like to join in the near future) and some documents of a declarative nature such as the Strategic Orientation on Waste Management in the Republic of Slovenia, the National Environmental Protection Programme and the like, which have not been implemented to the full extent or within the deadlines specified in the documents themselves. Unfortunately, many more years will have to pass before Slovenia's environmental policy will achieve a level equal to that in EU member states, or as envisaged by EU guidelines and directives.

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## SWITZERLAND

## 1. NEW ORDINANCE RELATING TO CHARGES FOR THE REMEDIATION OF POLLUTED SITES

The cost of remediation for about 3,000 contaminated sites in Switzerland over the next 20 to 25 years is estimated at about 3 billion Euro. The costs of decontamination are to be borne according to the "polluter pays" principle. However, since in many cases the polluter can no longer be traced or may be unable to pay, part of the cost has to be met by public funding. It is estimated that this requirement for public funding will amount to about 1.3 billion Euro.

To contribute to public funding of the remediation of polluted sites, on 5 April 2000, the Federal Council voted for the new ordinance relating to charges for the remediation of polluted sites, and this will come into force on 1 January 2001. A tax will be levied on landfill, and on the export of waste for landfill abroad, and this should bring in about 17 million Euro per year. The rates of taxation vary between 10 and 30 Euro per tonne of deposited waste. In principle, the federal government will refund to the cantons $40 \%$ of the decontamination costs that are to be met by public funding.

The main points covered by the ordinance are:

- the procedure for taxing landfilling with waste in Switzerland, and the export of waste for landfill abroad;
- the rates of taxation to provide about 17 million Euro per year to contribute to the decontamination of polluted sites where costs accrue to the community;
- the prerequisites and procedures for subsidising the cantons, in particular the level of subsidy and the costs of decontamination that can be taken into account.

Tax collected by virtue of this ordinance is to make a considerable contribution to the decontamination of polluted sites in a way that is acceptable from the environmental point of view, makes economic sense, and uses up-to-date technology, whilst being carried out rapidly and in a way appropriate to the degree of ecological urgency.

## 2. SUSTAINABLE REMEDIATION OF CONTAMINATED SITES

Over the past few months, the topic of contaminated sites has come to the fore, and one case has led to discussions at the ministerial level throughout Switzerland and abroad (Bonfol chemical waste landfill site in the Canton of Jura). Investigations on polluted sites and their decontamination are not only carried out in the context of construction plans, but also increasingly in places where there is an urgent need from the ecological point of view (i.e., without any relation to construction projects).

According to the Contaminated Sites Ordinance, which has been in force since 1998, the main goal of remediating polluted sites is the long-term prevention of unlawful emissions at source. This can be achieved either by decontamination or by securing/containment measures. At a first glance, it may often appear less expensive to make the site safe by containment measures, rather than carrying out decontamination.

However, especially for contaminated sites with persistent pollutants (e.g., chlorinated solvents), making the site safe can be much more expensive overall in the long term, as construction systems may need to be supervised and maintained for hundreds of years. Measures to ensure safety make sense if it can be guaranteed that after one or two generations the site can be left alone, without the need for further measures to be taken. This should be the case for readily degradable pollutants that can be absorbed, for instance mineral oils and for landfill sites containing municipal waste.

I should now like to describe briefly two important current examples of polluted sites that need to be decontaminated, each of which can be classified as a "persistent pollutants site" or PEPSI. The sites in question are the hazardous landfill sites of Bonfol and Kölliken.

## 3. CURRENT EXAMPLES OF WORK ON CONTAMINATED SITES

## Bonfol landfill site

This landfill site is located in the Jura Mountains near to the border with France. It represents a threat to groundwater and surface water on both sides of the border. This landfill site was used by the chemical industry of the Basle area from 1961 to 1975 , and contains about 114,000 tonnes of special chemical waste, in particular residues of the production of agrochemicals, dyes and pharmaceuticals. After the landfill site closed in 1975, it was sealed over, and a drainage system and wastewater treatment facility were installed. These safety measures cost 15 million Euro, with about 1 million Euro additional annual maintenance costs.

Based on the presence of persistent organic pollutants and heavy metals, it is predicted that it would take between 700 and 1,500 years until the site could be left to itself. Thus Bonfol represents a classical "persistent pollutants site" or PEPSI.

Based on legislation, the Swiss Agency and the Canton of Jura demanded a feasibility study, and it showed that it would be technically possible to carry out total decontamination of this site (i.e., excavation and thermal treatment of the wastes), and to deal with the waste in an environmentally compatible way. According to initial estimates, the cost of decontamination would be about 100 million Euro. From the economic point of view, decontamination should be less expensive in the long term than maintaining safety systems for several centuries. It should also be mentioned that it is only possible to ensure environmental protection for contaminated sites as long as the safety system remains in working order.

The chemical industry, which was the source of this environmental problem (i.e., the polluter), has declared that it is prepared to take on the decontamination of this site within a reasonable period of time.

## Kölliken landfill site

Kölliken landfill site is in the densely populated Swiss central plateau area, and it is one of the largest contaminated sites of Switzerland. It is the largest known PEPSI in Switzerland, and is located in hydrogeologically highly complicated surroundings. This landfill site was used from 1978 to 1985, and contains about 400,000 tonnes of hazardous waste from all regions of Switzerland.

To protect the valuable groundwater supply, about 100 million Euro have already been invested in safety measures, and the costs of operating the system are about 3 million Euro per year. Based on the quantity of persistent pollutants present and the current leaching and degradation processes, it is to be assumed that for this site too the safety system will need to be maintained for several centuries to a thousand years. The cost of this will be enormous.

In the meantime it has been decided, on a political and rational basis, that Kölliken landfill site has to be decontaminated/excavated. An original way was chosen to find the optimum solution for decontaminating the Kölliken site, namely a competition for ideas was opened. An international jury, including two representatives of the NATO-CCMS group, selected three of the ideas for decontamination that had been submitted, and these are now to be developed in greater detail.

The information available shows that differentiated excavation and treatment of hazardous material is possible, at a cost of about 200 to 300 million Euro. These costs are considerably less than estimates
made about fifteen years ago, when (faced with an estimate of 700 Euro for decontamination) safety measures were taken instead.

## Finally: a Swiss specialty

Within the domain of contaminated sites there has been increasing discussion about 300m-long shooting ranges and their logical contamination with spent ammunition over the past two to three years. There are more than 2,100 such ranges in Switzerland, as there is an obligation for active members of the army to do shooting practice till the age of 40 (actually more than 340,000 persons are concerned). Until a few years ago about 9 grams of lead ended up in the ground per shot, and nowadays the figure is about 4 grams. Civil and military shooting put about 500 tonnes of lead underground or into the soil each year. It is to be envisaged that, in the future, especially with the re-sizing of the army that is on the agenda, some of the lead-polluted shooting ranges will be decommissioned. Many communities would like to clear shooting ranges from any remnants of the shooting activities, and to treat the lead-contaminated material in an environmentally appropriate way. However, at present there are few acceptable, satisfactory solutions for treatment of such materials. The main options are soil washing and thermal treatment (recycling of lead), and landfill for material that is only slightly contaminated with lead.

## TURKEY

## 1. LEGAL AND ADMINISTRATIVE ISSUES

There is 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 $S W$ and $C$ of $H W$ regulations have 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 that 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.

## 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 AND RD\&D

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 at few chemical spill sites, pump and treat type technologies are being used for groundwater cleanup. Most probably these sites will set precedence, in terms of both cost and performance, for cleanup in other similar sites.

There is a pressing need for research and development of soil and groundwater cleanup technologies in Turkey. The number of soil and groundwater remediation research projects supported financially by the Turkish State Planning Organization, The Scientific and Technical Research Council of Turkey and other governmental institutions is increasing. For example, a project regarding the performance assessment of solidification/stabilization (S/S) technology for remediation of a large group of wastes (e.g., soils, mining residue and paper and pulp industry sludge) containing organic contaminants (PCB and AOX) and heavy metals has been initiated. The main purpose of this project is to investigate the reliability of $\mathrm{S} / \mathrm{S}$ technology for remediation of certain waste groups and provide technical and economical guidance for its field-scale applications. The General Directorate of State Hydraulic Works is about to finish a couple of pilot projects to update hydrogeologic investigations of two major groundwater basins. The main objectives are to develop comprehensive database and appropriate groundwater management plans using recent technologies such as GIS, RS and advanced numerical groundwater modeling and to set the standards for similar studies for the other major basins.

## 4. 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 has 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

## 1. LEGAL AND ADMINISTRATIVE ISSUES

At the first two meetings of the Pilot Study, the 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 fully described.

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. 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, it is anticipated that the provisions of the 1990 Act will come into force in mid-July.

More 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 certain 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 importance of urban regeneration and the beneficial reuse of brownfield land continue to be a major topic of debate in the UK. In June 1999, the Government appointed Urban Task Force reported its conclusions and recommendations about reversing urban decline in England after a 14-month study. The challenges posed by dealing with land contamination represented a significant issue in the brownfield debate. In considering the issues, the report concluded that:

- Most contaminated land is capable of safe remediation using modern technology at reasonable cost.
- The present barriers to redevelopment are largely to do with the perception of risk.
- There is a need to simplify and consolidate the regulatory systems that seek to protect the environment from the consequences of contamination.
- There is a need to promote greater standardisation in the way that the UK manages the risks involved in redeveloping contaminated sites, and thereby promote a better and consistent understanding of the situation.


## 2. TECHNOLOGY DEVELOPMENT PROGRAMMES

At the last Pilot Study meeting in Angers, France, the launch of CLAIRE (Contaminated Land: Applications in Real Environments) was reported. The objective of CLAIRE is to establish a network of test sites to research and demonstrate cost-effective techniques for the investigation and remediation of land affected by contamination in the UK. It aims to address the key issue of how to get over the information barrier limiting the use of process-based remediation technologies in the UK.

In the past year, CLAIRE has received 11 applications for research and demonstration projects. The first CLAIRE Technology Demonstration project involved field-scale trials of low temperature thermal desorption (LTD) technology carried out on 40 tonnes of hydrocarbon-contaminated soil. The project report will be available shortly. CLAIRE is currently working with site owners to develop the range of sites that might be available to the network for remediation projects-current discussions involve about 50 sites. In addition, the Technology and Research Group (TRG) within CLAIRE has been finalising the key aspects of the CLAIRE Research Strategy. CLAIRE can be reached on the web at www.claire.co.uk.



Civil engineering methods were used on nearly all sites. Processbased techniques were not used exclusively but in combination with civil engineering methods. Key techniques used include SVE, DVE, ex situ bioremediation, and soil washing.

It should be noted that more than one category of contaminant might appear on the same site.

The contaminants identified are likely to be the "risk-driver" compounds (i.e., the most memorable) and others may have been present.

## 3. REMEDIAL METHODS IN USE

At the last Pilot Study meeting in Angers, France, it was reported that the Environment Agency had commissioned a survey of remedial techniques that had been used in England and Wales for remediation in recent years. This survey has now been completed and the report will be published in the next few months [3]. However, it has been possible to illustrate some of its findings here.

In total, more than 1,500 sites were identified by the survey where remediation was carried out during the period January 1996 to December 1999. The amount of information collected about each site varied considerably. The majority of sites:

- Were small sites less than 5 hectares in size.
- Resulted from development led remediation (with most involving a change of use from industrial to residential).
- Involved civil engineering-based remediation techniques (largely excavation and disposal, minor regrading, and caps/cover systems).

However, the survey also found evidence that multiple remediation techniques are being used on sites to match contaminant distribution patterns, end-use layout, and the drive to minimise costs. Although only a minority of sites was found to be subject to formal options appraisal there was evidence that cost, while being a key consideration, was not the only factor taken into account. Cost data was found to be extremely difficult to collect.

The charts on the following page illustrate some of the preliminary findings of the survey.

## Research and Development Activities

Table 1 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 1: Recent UK R\&D Projects on remediation of land affected by contamination (not intended to be inclusive)

| PROJECT | STATUS |
| :--- | :--- |
| RESEARCH COUNCILS | Published in 2000. <br> Available from the Institute of Terrestrial <br> Ecology, Furzebrook Research Station, <br> Wareham, Dorset, BH20 5AS, United Kingdom |
| Disposal of Oiled Beach Sand in Coastal Soils. | Supported by the Maritime Coastguard Agency <br> and the Natural Environment Research Council |
| Dual anaerobic system for bioremediation of <br> metal/organic wastes | BBSRC <br> Professor Macaskie, University of Birmingham |
| Bioremediation and microbial population <br> dynamics | BBSRC <br> Dr Head, University of Newcastle |
| Cyanide biodegradation: a model for the <br> development of molecular probes for <br> optimisation of bioremediation | BBSRC <br> Professor Knowles, University of Oxford |
| Phytoremediation: an integrated biological <br> approach to the decontamination of polluted soils | BBSRC <br>  <br> Environmental Microbiology |
| An integrated, multifunctional system for <br> bioremediation of waters containing xenobiotics <br> and toxic metals | BBSRC <br> Professor Livingston, Imperial College of <br> Science, Technology, and Medicine |
| Non-invasive characterisation of NAPL- <br> contaminated land by spectral induced <br> polarisation (SIP) tomography | EPSRC / NERC <br> Dr. Ogilvy, British Geological Survey |
| New sensor system for monitoring solvent <br> migration from contaminated sites | EPSRC/NERC <br> Professor Williams, University of Central <br> London |
| Studies into metal speciation and bioavailability <br> to assist risk assessment and remediation of <br> brownfield sites in urban areas | EPSRC/NERC <br> Professor Thornton, Imperial College of Science, <br> Technology, and Medicine |
| In situ sensing of the effect of remediation on <br> available metal fluxes in contaminated land | EPSRC/NERC <br> Professor Davison, University of Lancaster |


| Bacterial biosensors to screen in situ <br> bioavailability, toxicity, and biodegradation <br> potential of xenobiotic pollutants in soil | NERC <br> 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 $\quad$ Published in November 1999.
Contamination
To provide advice on assessing the costs and benefits of different remedial techniques as part of a selection process
Natural Attenuation of Petroleum Hydrocarbons and Chlorinated Solvents in Groundwater

To provide a review of current knowledge on natural attenuation of two common organic pollutants in groundwater systems: petroleum hydrocarbons and chlorinated solvents.
Costs and Benefits Associated with Remediation of Contaminated Groundwater: A Review of the Issues.

To provide guidance on the issues associated with the costs and benefits of remediating contaminated groundwater.
Some 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.

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. 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.

R\&D Technical Report P316.

Published in December 1999.

R\&D Technical Report P305.

Published in December 1999.

R\&D Technical Report P278.

Published in March 2000.

R\&D Technical Report NC/06/32.
Prepared in collaboration with the British
Geological Survey.
Published in June 2000.

R\&D Publication 66.
Prepared in collaboration with the National House Building Council.
Published in 2000.

R\&D Technical Report P331.

| Assessing the Wider Environmental Value of <br> Remediating Land Contamination: A Review. <br> To review the international approach to assessing <br> the wider environmental effect of different <br> remedial strategies as part of a selection process | R\&D Technical Report P238. |
| :--- | :--- |
| Guidance on the Assessment and Monitoring of <br> Natural Attenuation of Contaminants in <br> Groundwater | Project completed (available shortly). |
| To provide guidance on the assessment and <br> monitoring of natural attenuation of contaminants <br> in groundwater. | R\&D Publication 95. |
| Site for Innovative Research on Natural <br> Attenuation (SIREN) | On-going project. |
| To study the application of natural attenuation at <br> a specific site and to encourage and disseminate <br> the outcome of projects to benefit our wider <br> understanding of the applicability and <br> implementation of natural attenuation. |  |
| Guidance on monitoring the Operational and <br> Post-Remediation Performance of Remedial <br> Treatments for Land Contamination | On-going project. |
| To provide guidance on the monitoring <br> requirements for land remediation |  |
| Verification of remedial treatments | On-going project. |
| To develop guidance for the verification of <br> different remedial techniques to enable <br> performance to be established during remediation <br> and after works have been completed |  |
| Development of Appropriate Soil Sampling <br> Strategies for Land Contamination | On-going project. |
| To develop guidance to assist the design of a site <br> investigation strategy in accordance with the site <br> conceptual model and the data requirements for <br> risk estimation and evaluation. |  |
| Field study of the performance of cover systems <br> for land remediation | New start in 2000/01. |
| To provide baseline field evidence for the long- |  |
| term performance of cover systems to improve |  |
| regulatory confidence in their appropriate |  |
| application. |  |$\quad$.


| A review of remedial options for DNAPL source treatment <br> To review the international experience of source treatment of DNAPL contaminants to evaluate information transfer and prioritisation of research into the UK. | New start in 2000/01. |
| :---: | :---: |
| Valuation of environmental benefits of remediation techniques in relation to land contamination <br> To evaluate the feasibility for semi-quantitative assessment of the environmental benefit resulting from the remediation of land contamination (including different remedial techniques). | New start in 2000/01. |
| A study of the long term management practices and perceptions of remediated contaminated sites <br> To study long-term management practices and perceptions of remediated contaminated sites to improve our understanding of current practice and the effectiveness of current guidance. | New start in 2000/01. |
| SCOTLAND AND NORTHERN IRELAND FOR <br> Reports are available from the Foundation for Wa Road, Marlow, Bucks SL7 1FD, UK. | UM FOR ENVIRONMENTAL RESEARCH research, Allen House, The Listons, Liston |
| Protocol and Guidance Manual for Assessing Potential Adverse Effects of Substances on Designated Terrestrial Ecosystems <br> 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 <br> To provide guidance on deriving site-specific assessment criteria for unacceptable chronic risk to human health. | Published in January 2000. <br> Report No. SR99(02)F. |

## CONSTRUCTION INDUSTRY RESEARCH AND INFORMATION ASSOCIATION

Remedial Engineering for Closed Landfill Sites. $\quad$ Funders Report CP/61.
To provide guidance on the range of options for restoring closed landfill sites to a range of different end uses.

For information contact CIRIA at 6 Storey's Gate, Westminster, London, SW1P 3AU.

| Remedial Processes for Contaminated Land: <br> Principles and Practice. | Funders Report R000. |
| :--- | :--- |
| To provide good practice guidance on the <br> selection and implementation of certain <br> categories of process-based technologies. | For information contact CIRIA at 6 Storey's <br> Gate, Westminster, London, SW1P 3AU. |
| Contaminated Land: Financial Control of Risk. | Funders Report. |
| To provide guidance to those involved in the <br> redevelopment of brownfield sites on how to <br> manage and limit the financial risk posed. | For information contact CIRIA at 6 Storey's <br> Gate, Westminster, London, SW1P 3AU. |
| Contaminated land: in-house training material <br> To produce training package aimed at the <br> construction industry to raise awareness of the <br> application of a range of remedial techniques and <br> approaches to risk assessment. | On-going project. |
| Biological treatment for contaminated land: case <br> studies. | New start in 2000/2001. |
| To disseminate information on good practice <br> using biological treatments in the UK. |  |
| Client's guide for building on brownfield sites. | New start in 2000/2001. |
| To provide guidance to the construction industry <br> on adopting a sustainable approach to building on <br> contaminated sites. |  |
| Safe working practice on contaminated land - <br> training material. | New start in 2000/2001. |
| To provide training for those responsible for site <br> safety and construction staff working on <br> redevelopment of land affected by contamination. |  |

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## 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 September 30, 1999, over 397,000 confirmed releases had been reported, over 346,000 cleanups initiated, and over 228,000 cleanups completed.

## 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 May 2000, EPA has authorized 34 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.

## Anticipated Policy Developments

As debate continues on legislative changes to Superfund, there have been efforts to streamline the RCRA Corrective Action program. EPA issued regulations simplifying the permitting process and modifying land disposal restrictions for cleanups. EPA has also launched an initiative to expedite actions through new guidance, rulemaking and public outreach. The Corrective Action program has set goals for the 1700 high priority facilities. The goals include control of human exposure at 95 percent of sites and control of ground-water migration at 70 percent of facilities by the year 2005.

There is widespread and growing interest in using risk assessment to determine cleanup priorities, as may be done under the Risk Based Corrective Action initiative in the UST program. There is also increasing
interest in the issue of bioavailability of contaminants as an alternative to chemical concentrations alone to set cleanup standards. Much scientific work and consensus building has yet to be completed on this issue.
"Brownfields" initiatives have also 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 100,000 to 450,000 such sites in the United States. A growing realization of their great potential has heightened interest in their cleanup and redevelopment. EPA has funded over 300 Brownfield Assessment Pilots and 16 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 98 Brownfields Cleanup Revolving Loan Fund grants for up to $\$ 500,000$. In addition, EPA has provided Brownfields job training and development grants to 37 communities to provide environmental training for residents near the sites. Also, a $\$ 1.5$ billion Brownfields tax incentive has been enacted to further encourage cleanup and redevelopment.

## 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. REMEDIATION TECHNOLOGIES

## Historical Remedial Technology Use in the U.S.

The most comprehensive information on technology use at waste sites is available for the Superfund program. Although they represent a small percentage of all contaminated sites, technology selection is representative of other hazardous waste sites. After reauthorization in 1986, most remedies involved some treatment of contaminated soil, as opposed to containment or off-site disposal. However, in 1993 the percentage of sites selecting some treatment began to decrease. In 1996, the number of containment or off-site disposal projects exceeded the number of source control treatment remedies chosen for the first time since 1986. The selection of treatment has stabilized in the last two years.

When treatment is selected, there is a trend toward greater use of in situ processes, as shown in the figure. In 1996, in situ technologies made up 66 percent of source control technologies in the Superfund program. Because there is no excavation, these technologies pose a reduced risk from exposure and can result in considerable cost savings, especially for large sites.

The most frequently selected treatment technologies for source control have been soil vapor extraction (SVE), solidification/stabilization and incineration. These technologies are followed by bioremediation and thermal desorption. Three-quarters of these remedial projects address only organics, while the remainder address either metals alone or in combination with organics.

Ground water is contaminated at 70 percent of Superfund sites. Despite recent advances, 89 percent of remedies selected for controlling ground-water plumes rely on conventional pump-and-treat technologies, 6 percent use in situ treatment in addition to pump-and-treat, and 5 percent utilize in situ technologies alone. The most frequently selected processes include air sparging, bioremediation, and dual-phase extraction. Many of the treatment technologies have only recently been selected and much work is underway to develop and test new processes. One recently developed process involves permeable reactive barriers, which have been rapidly deployed at full-scale. Early applications involved zero-valent iron to
treat chlorinated solvents. Research and demonstration is focusing on materials to treat other contaminants such as chromium, polynuclear aromatic hydrocarbons (PAHs), and radionuclides. Natural attenuation has been used extensively to address petroleum contamination from underground storage tanks. This approach relies primarily on naturally occurring biodegradation of contaminants in the subsurface. It is also being selected at hazardous waste sites, but primarily as a final polishing step as opposed to a sole remedy for a site.

Control of ground water plumes alone cannot always meet desired cleanup goals because of the presence of NAPLs (non-aqueous phase liquids). The three most prominent technologies for treating DNAPL (dense non-aqueous phase liquid) include three in situ processes: oxidation, flushing and thermal 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 so present at many sites.

## 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 is probably the single most important factor affecting our ability to attain cleanup levels in ground water. Despite relatively few projects employing DNAPL treatment technologies, very important results were reported using steam extraction at a wood-treating site in Visalia, California. Pumping and treating was removing about 10 pounds of creosote per week. Using in situ steam enhanced thermal treatment, over one million pounds of DNAPL were recovered in the first two years of operation. These results have generated optimism in terms of our ability to address prevalent DNAPL problems and helped encourage an important demonstration project to concurrently evaluate three in situ technologies. This project involves a TCE (trichloroethylene) DNAPL problem resulting from a spill at an old launch pad at Cape Canaveral, Florida. The project, led by the National Aeronautics and Space Administration with support from the Air Force, DOE and EPA, should provide comparative data for three selected in situ processes: six-phase thermal heating, steam injection and oxidation. The sixphase heating and oxidation fieldwork has been completed and the steam injection effort is scheduled to begin soon. At another level, member agencies of the Federal Remediation Technologies Roundtable have agreed to coordinate efforts to speed the maturation of DNAPL technologies. Work Groups are being established to improve coordination on research and information sharing from demonstration and full-scale applications.

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 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.

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. 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 developed a procedure for screening sites to determine if more detailed application of optimization software is warranted. Federal agencies are developing programs to identify opportunities to realize cost
savings while maintaining acceptable levels of risk. Optimization is capable of producing substantial savings.

As an alternative to pump-and-treat systems, monitored natural attenuation is receiving a lot of attention. 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.

A significant new challenge is resulting from the recent emergence of MTBE (the gasoline additive methyl tertiary butyl ether), which is a contaminant being found with alarming frequency in ground-water supplies around the country. 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.

## 4. RESEARCH, DEVELOPMENT, AND DEMONSTRATION

Federal agencies currently are coordinating several technology development and commercialization programs. DOE is spending $\$ 238$ million in Fiscal Year 2000 to develop new environmental cleanup technologies. A DOE report released this year describes 20 new technologies that may lead to cost savings in cleaning up DOE sites. These technologies are specific examples of the types of technologies that DOE expects to need in the near future, such as bioremediation, electrokinetics, and biosorption of uranium.

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 $\$ 15$ million per year. The Strategic Environmental Research and Development Program (SERDP) is a joint program with DOD, DOE, and EPA-funded at $\$ 61.8$ million per year, which devotes 31 percent of its resources to remediation and site characterization technologies. DOD's high priority cleanup technology needs include: detection, monitoring and modeling (primarily related to unexploded ordnance [UXO] and DNAPLS); treatment for soil, sediment, and sludge (primarily related to UXO, white phosphorous contaminated sediments, inorganics, explosives in soil, explosives/organic contaminants in sediments); groundwater treatment (explosives, solvents, organics, alternatives to pump-and-treat, and DNAPLs); and removal of UXO on land and under water.

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 potential users can assess applicability to a particular site. A similar program that 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 www.epa.gov/ORD/SITE and www.epa.gov/etv. The publication source for EPA documents is 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 seven action teams, which are co-chaired by a government and industry representative. 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 78 new studies of full-scale remediation and demonstration projects. This added to 140 studies that were published previously. The reports are available on the Roundtable's web site (http://www.frtr.gov) with a user-friendly search capability. 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.

## 5. CONCLUSIONS

Legislative, regulatory and programmatic changes may alter the nature and sequence of cleanup work done at Superfund, RCRA, DOD, and DOE sites. Other than focused Brownfields legislation, no major reauthorization of either the Superfund or RCRA programs is anticipated this year. EPA will continue implementing administrative reforms and refining or improving them where necessary. EPA does support new provisions that would provide targeted Superfund liability relief to qualified parties such as prospective purchasers, innocent landowners, contiguous property owners, and small municipal waste generators and transporters.

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 aboveground 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.

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## PILOT STUDY MISSION

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." 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 pilot study draws from an extremely broad representation and the follow up would work to expand this.

The current study has 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 re-use 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. ESTIMATED DURATION

November 1997 to November 2002 for meetings.
Completion of final report: June 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 a 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.

| Pilot Country: | United States of America |
| :--- | :--- |
| Lead Organization: | U.S. Environmental Protection Agency |

U.S. Directors:

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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

Scheduled Meetings: February 23-27, 1998, in Vienna, Austria May 9-14, 1999, in Angers, France June 26-30, 2000, in Wiesbaden, Germany 2001 in Canada or the United States

