NATO/CCMS Pilot Study

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

Interim Status Report

Number 203
NORTH ATLANTIC TREATY ORGANIZATION
NOTICE
This report was prepared under the auspices of the North Atlantic Treaty Organization's Committee on
the Challenges of Modern Society (NATO/CCMS) as a service to the technical community by the United
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NATO/CCMS Pilot Study

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May 1995
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INTRODUCTION

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

The management of contaminated land and groundwater is a universal problem among industrialized countries, requiring new and improved remedial technologies. This document provides an interim status report on the second phase of a Pilot Study designed to share information among countries on innovative treatment technologies. The United States is the lead country for the Pilot Study, and Germany and the Netherlands are Co-Directors. The first phase successfully concluded in 1991, and the results were published in three volumes. The second phase continues to address field-demonstrated technologies while expanding the scope to include newly emerging technologies. Through these pilot studies, critical technical information has been made available to participating countries and the world community.

The first meeting of the NATO/CCMS Phase II Pilot Study on the Treatment and Cleanup of Contaminated Land and Groundwater convened in Budapest, Hungary, on October 18-22, 1992. The second meeting was in Québec City, Canada, on September 12-17, 1993. The most recent meeting was in Oxford, United Kingdom, September 11-16, 1994. Summary reports for each of these meetings are available through the Country Representative listed at the end of this report.

Each participating nation may report on up to four active case studies in the Pilot Study at any one time. As studies are completed, new projects may be added. At the end of the Phase II Pilot Study, a final report will be published that provides technical documentation for all projects. Because the Phase II Pilot Studies will continue for another two years, this interim report was prepared in order to share technical information as quickly as possible.

This report is divided into four parts. The first part contains abstracts of each of the technical case studies sanctioned by the Pilot Study prior to September 1994. Each abstract is headed by a summary table that provides pertinent data at a glance. Most of the studies are still in progress; those that are completed are so noted in the accompanying abstracts. A guide to the information contained in each abstract header may be found on the next page. The summary table on page v provides an overview of the technology types, affected media, contaminants, project status, and sponsoring country for each case study. The second part of the report contains preliminary information on 15 projects newly accepted by the Pilot Study in September 1994. The table on page 30 provides an overview of these projects.

Although case studies are the primary focus of the Pilot Study, two other activities also provide opportunities for technical exchanges. The third part contains summaries of guest presentations of general interest made at Pilot Study meetings. The fourth section of this report contains a brief description of NATO fellowships projects. These fellowships provide only travel funds to researchers who are pursuing topics of relevance to NATO Pilot Studies.

Further information on specific projects may be obtained from the individual technical contacts (listed for each abstract) and general information on the NATO/CCMS Pilot Study from the country representatives listed at the end of this report.

Stephen C. James
Walter W. Kovalick, Jr., Ph.D.
Co-Directors
# LEGEND AND NOTES

<table>
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<th>Project Title</th>
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<tbody>
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<td>Location</td>
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<td>Project Status</td>
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<td>Contaminants</td>
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<tr>
<td>Results Available?</td>
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1 Title of project presented at the Oxford Conference, September 1994. (The same project may have had a different title in earlier meetings at Budapest or Québec City.)

2 The site at which the pilot project occurred. If the project was a laboratory-scale project, the name of the laboratory. If no geographic specificity was indicated, the name of the Country sponsoring the study.

3 If the final report was presented at the Oxford or Québec meetings, the status is “Final.” If the project is on-going, the status is “Interim.” Projects accepted at the Oxford meeting are labelled “New.”

4 Contaminant groups include: Total Petroleum Hydrocarbons/BTEX (benzene, toluene, ethylbenzene, xylene); chlorinated volatiles; chlorinated semivolatiles (such as PCBs); nonchlorinated semivolatiles (polycyclic aromatic hydrocarbons PAHs); heavy metals and radionuclides.

5 Technology types include: bioremediation (in situ or ex situ); soil washing (including other physical processes); stabilization/solidification; soil vapor extraction; pump-and-treat; photochemical.

6 Name, affiliation, and telephone/fax numbers for the first author or other technical contact for the project.

7 Remediation/project dates, if provided.

8 Contaminated media categories include: soil/sludge/sediment; groundwater (including the saturated zone and pore spaces); surface water; air.

9 If project costs are available in the documentation, the answer is “yes.” If no costs were discussed, the answer is “no.” Costs, when given, are in the monetary units of the author.

10 The scale is provided as either “bench” (or laboratory), “pilot,” or “full.” Bench-scale means laboratory modeling or testing; pilot scale means field equipment at a smaller capacity for testing purposes; full scale means at production/commercial level. If geographic extent or contaminated volume is discussed, that number or range is provided.

11 If a written paper is available, the answer is “yes.”
<table>
<thead>
<tr>
<th>Title</th>
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<td>Field Demonstration of an In Situ Treatment Using Well Points</td>
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<td>Modeling and Optimization of In Situ Remediation</td>
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<td>Combined Remediation Technique Fortec®</td>
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<td>In Situ Microbial Filters</td>
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<td>Demonstration of Peroxidation Systems, Inc.</td>
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PILOT PROJECTS

<table>
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<tr>
<th>Project Title</th>
<th>Trial of Air Sparging of a Petroleum (Gasoline) Contaminated Aquifer</th>
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<tr>
<td>Location</td>
<td>Gasoline service station, Adelaide, South Australia</td>
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<td>Project Status</td>
<td>Final report (test)</td>
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<tr>
<td></td>
<td>Interim report (full-scale remediation)</td>
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<td>Contaminants</td>
<td>VOCs: BTEX</td>
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<tr>
<td>Technology Type</td>
<td>Soil Vapor Extraction with Air Sparging</td>
</tr>
<tr>
<td>Technical Contact</td>
<td>Ian A. Hosking</td>
</tr>
<tr>
<td></td>
<td>Coffey Partners Intl Pty Ltd.</td>
</tr>
<tr>
<td></td>
<td>North Ryde, NSW Australia</td>
</tr>
<tr>
<td></td>
<td>tel: 61/2-888-7444</td>
</tr>
<tr>
<td></td>
<td>fax: 61/2-888-9977</td>
</tr>
<tr>
<td>Project Dates</td>
<td>Tests: September 1993</td>
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<tr>
<td></td>
<td>· April 1994</td>
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<td>Remediation: January 1994 onward</td>
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<td>Media</td>
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<td>Project Size</td>
<td>Pilot scale</td>
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<td>Results Available?</td>
<td>Yes</td>
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</table>

While air sparging substantially increased the amount of volatile hydrocarbons that can be removed by vapor extraction in the short term, the rate slowed dramatically within just a few days. This appears to be due to relatively low permeability at the site, and the formation of preferential flow paths for sparged air. Future remedial efforts should make use of lowering the water table and extracting vapor through the vadose zone rather than air sparging.

A 30-year old service station leaked gasoline into the soil as a result of faulty piping. Testing found 2,100 mg/L total hydrocarbons (THC), including an estimated 200,000 kg of BTEX contamination in the “smear zone” around the water table. A remediation strategy involving soil vapor extraction with air sparging below the water table was selected because it is an in situ technology, obviating the need for surface water treatment and disposal. Since air sparging is a relatively new technology, three trials were conducted prior to full remediation. This project is the first non-pump-and-treat technology for groundwater to be included in the NATO/CCMS Phase II Pilot Study.

The first air sparging trial consisted of three vapor extraction wells arranged in a triangle and one injection well at the center. Vacuum levels of 15-20 kPa resulted in an air permeability of $10^{-7}$ cm$^2$/sec, and is on the high end of the expected range for the sandy layer above the water table. Injecting air resulted in increased extraction of THC vapor from the extraction wells. The second test, conducted about a month later, also involved vacuum extraction with and without air sparging. Total concentrations of extracted HC and BTEX compounds were substantially increased (often 10-fold) by air injection. Injection of air into one extraction well also resulted in a greater rate of HC extraction than when vacuum was maintained without air injection. The system was estimated to extract between 0.04 and 0.1 kg/hr of THC, or between 1 and 3 kg/day. However, a third trial was conducted six months later to measure THC recovery rates as a function of time. The third trial also monitored HC and O$_2$ stack emissions, DO concentrations in the groundwater to assess sparging with distance, gaseous O$_2$ concentrations in background wells as an indication of microbial activity, groundwater levels, and power.

The short second trial and the first 48 hours of the third trial resulted in extracted air (stack) concentrations of 100-150 ppm (and as high as 300-600 ppm) of total volatile HC. However, the relatively high extraction rates achieved in the first two days were not sustained. A sudden decline in HC extraction concentrations after 8 hours of extraction and about 50 hours of sparging was attributed to removal of HC from the immediate vicinity and the removal of HC from the more permeable layers. In the third trial, injection of air down one of the extraction wells did not increase extracted HC as it apparently did during the earlier test. The zone of influence of air sparging affects the spacing of the sparging bores and therefore the cost. Results indicated a remediation influence of 3-9
m from the injection well. Air sparging induces water table mounding at the injection well (noticed from 3-10 m), increasing groundwater flow from the well. Soil layering also creates horizontal flow paths. The lack of hydrocarbons reaching extraction wells late in the trial suggests that air followed preferred pathways that were more readily cleansed of volatile HCs, which then acted as conduits for relatively clean injected air. Soil O$_2$ monitoring was inadequate to quantify microbiological activity during or after the trial. Concentrations of O$_2$ increased from 10.5% to 19-21% during sparging. Relatively little injected O$_2$ was consumed by soil bacteria. The concentration of O$_2$ in the extraction exhaust was only 10% at the start of sparging, and probably indicates the presence of active hydrocarbon-degrading bacteria in the smear zone.

---

**Project Title**

Technical and Economic Aspects of *In Situ* Bioremediation

<table>
<thead>
<tr>
<th>Location</th>
<th>Project Status</th>
<th>Contaminants</th>
<th>Technology Type</th>
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<tbody>
<tr>
<td>Austria</td>
<td>Interim Report</td>
<td>Organics</td>
<td><em>in situ</em> bioremediation</td>
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<th>Technical Contact</th>
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<td>Werner Erhart-Schimpke</td>
<td>N/A</td>
<td>Soil, sediment</td>
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<td>Abelegasse 8 1160 Vienna Austria</td>
<td></td>
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<tr>
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<th>Project Size</th>
<th>Results Available?</th>
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<tbody>
<tr>
<td>No</td>
<td>Laboratory/field scale</td>
<td>No</td>
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*In situ* bioremediation of contaminated sites has the advantage of not having to move the contaminated soil to the place of treatment. Effective use of *in situ* bioremediation requires extensive experience in hydrogeology, chemistry and microbiology. In Austria, the estimated number of possible old landfills is about 3500. Many of these are former industrial plants with organic compound contaminated soil.

The objective of this project is to discover all the limitations of *in situ* bioremediation starting with bench scale tests and going on to field studies. Aspects of interest are the hydraulic, geotechnical and microbiological influences on biodegradation. The study will be divided into 5 steps. In step one the biodegradation of mineral oil products in five different soils will be analyzed simulating the saturated and the unsaturated zone. In step two the biodegradation of different organic compounds in a permeable soil with differing methods of aeration will be tested.

The results of steps one and two will dictate the methods used in step three where a scale-up to reactors of up to 30 m$^3$ volume will be used to simulate real field conditions.

A second objective of the study is to develop a testing procedure for application of *in situ* bioremediation of contaminated soils. In addition the costs will be evaluated as a basis for financial calculations and comparing different variants of remediation.

It is intended that the whole project will last for three years.
<table>
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<tr>
<th>Project Title</th>
<th>Demonstration of Thermal Gas-Phase Reduction Process</th>
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<tr>
<td>Location</td>
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<td>Doug Hallett</td>
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<td>ELI Eco Logic Intl, Inc.</td>
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<td></td>
<td>143 Dennis Street</td>
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<tr>
<td></td>
<td>Rockwood</td>
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<tr>
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<td>Ontario, N0B 2K0, Canada</td>
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<td>Project Size</td>
<td>Pilot scale</td>
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This patented process involves the gas-phase reduction of organic compounds by hydrogen at elevated temperatures to convert aqueous and oily hazardous contaminants into a hydrocarbon-rich gas phase. Soils are handled within a thermal desorption mill (TDM), which is operated in conjunction with the reduction reactor. Chlorinated hydrocarbons, such as polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins (dioxins) are chemically reduced to methane and hydrogen chloride (HCl), while non-chlorinated organic contaminants, such as polyaromatic hydrocarbons (PAHs), are reduced substantially to methane and minor amounts of other light hydrocarbons. The HCl produced can be recovered as acid or scrubbed out in a caustic scrubber downstream of the process.

A pilot-scale process plant was tested for the first time at Hamilton Harbour, Ontario, in 1991. The waste processed during these tests was harbour sediment contaminated with coal-tar at concentrations of up to 300 g/kg (dry weight). Destruction removal efficiencies (DREs) of 99.9999% were calculated based on the total organic input and the PAHs analyzed in the boiler stack emissions. During one test, the liquid waste input was spiked with PCBs to create a waste with a PCB concentration of 500 mg/kg. A PCB DRE of at least 99.9999% was achieved.

A second series of pilot-scale tests was conducted in 1992 in Bay City, Michigan, as part of the U.S. EPA's SITE program. The wastes processed included oily PCB-contaminated water, high-strength PCB oil, and PCB-contaminated soil. Once again, DRE of 99.99% or greater were achieved. SITE Program Project Bulletins and a Technical Evaluation Report have been published.

Following the Bay City SITE demonstration, several significant improvements were made to the thermal desorption unit in order to increase its overall efficiency in allowing the desorption of contaminants from soils. The TDM has achieved excellent results in lab-scale tests, with PCBs in soils and sediments being desorbed from high ppm levels down to low ppb levels, which are orders of magnitude below disposal criteria.

A commercial-scale system (SE25) has been designed with a capacity to process 100-300 tonnes/day of contaminated soil or sediment and 20 tonnes/day of PCB askarel fluid. One similar unit is being used in Australia for the purpose of destroying obsolete pesticides.
An in situ remedial process combining soil flushing and bioremediation will be evaluated in a field scale demonstration project sponsored by Serrener/Varisco Consortium, the National Research Council of Canada, Environment Canada, and the Ministry of Environment of Quebec. The process is based on a wellpoint system developed by VARISCO SPA for the control of the water table in construction projects. The site being tested has a very low permeability (average of $10^{-6}$ cm/sec) and is contaminated with aliphatic and BTEX hydrocarbons.

The proposed treatment scheme is a two-stage process. After installation of the wellpoints a surfactant/co-surfactant solution is circulated through the contamination zone and recovered at the surface. The contaminated washings are passed through an effluent treatment plant. After recovery of the “soluble” fraction of the organic contaminants the wellpoints are used to inject nutrients, microorganisms (as necessary), and provide aeration for in situ bioremediation as the second stage of site clean up. It is proposed that the aeration be provided either by the injection of hydrogen peroxide or by pumping air through the wellpoints.

The project has been divided into four steps: laboratory scale selection of surfactants; in situ soil washing tests using the surfactant identified in lab tests; in situ biodegradation testing of residual hydrocarbons and the contaminated washing solution; and subsequent monitoring to verify if soils have been decontaminated.

The first step has been completed with the testing of over 50 types of surfactant and co-surfactant to establish which pairings, and at what concentrations, were effective at extracting over 95 percent of the hydrocarbons from the contaminated soil. Toxicity of the surfactants to degrader organisms has yet to be reported. Analysis of on site microbial activity and the identification of specific degrader organisms has been conducted. BTEX and aliphatic hydrocarbon degraders were identified.

The second part of the project has been performed at the field scale in order to specify and optimize operating parameters of the in situ process. The results show that surfactant use has no detrimental effect on soil and underground water microflora. Moreover, the surfactant use has no effect on ecotoxicological parameters such as photobacterium, phosphoreum, and algae toxicological assays. The third and fourth steps will take place in the summer of 1995.
The Daramend™ technology is reported in this overview to represent a major advancement in treatment of soil contaminated with organic pollutants both in terms of reduction of contaminant concentrations as well as removal of soil toxicity.

The Daramend™ bioremediation technology uses solid-phase, biodegradable organic amendments prepared to specific particle size ranges and nutrient profiles, low-intensity tillage of the soil/sediment, and maintenance of an optimal soil/sediment water content. Previous studies have indicated that soils containing more than 300-400 mg PCP/kg may be too toxic for direct bioremediation, requiring preliminary treatments such as soil washing. Extensive laboratory testing with a wide range of soils contaminated with wood treatment chemicals has proven the Daramend™ technology effective in soils containing up to 2,170 mg/kg PCP, with residual concentrations as low as 0.7 mg/kg PCP. Since the previous report in Québec, the emphasis has been on proving the technology at full scale.

Implementation of the Daramend™ technology is based upon achieving a homogeneous distribution of the organic amendment throughout the contaminated soil. A full-scale demonstration consisted of treating 1,500 T on-site and 3,500 T in situ to a depth of 60 cm. Full-scale on-site treatment reduced chlorinated phenol concentrations from 102 ppm to 35 ppm in 35 days and to 1.63 ppm after 175 days. On-site Daramend™ treatment reduced total soil PAH concentrations from an initial 619 ppm to 224 ppm after 35 days and to 79.1 ppm after 251 days. Degradation of specific PAH compounds all achieved Canadian standards for industrial soil.

During the past two years, the Daramend™ technology has been applied to over 50 soils with varying physical/chemical characteristics. Treatment times reflect the chemical and initial concentrations, but range from 90 days for heavy oil at contaminations of over 2,000 ppm up to over 200 days for similar concentrations of PCPs and most refractory large PAHs at 40-400 ppm. Degradation rates for total PAHs are dependent upon the degradation rates of the more refractory (4-6 ring) PAHs. Total PAHs were reduced from 1442 mg/kg to 36 mg/kg while refractory PAHs were reduced from 1248 mg/kg to 34 mg/kg in 209 days of Daramend™ treatment.

Three established bioassays were used to determine whether a corresponding reduction in soil toxicity was attained. The Microtox™ toxicity test was performed on soil and soil leachate, and toxicity was reduced by two orders of magnitude in the leachate and by a factor of about 40 in soil. The earthworm mortality test resulted in 100% mortality within 4 days in untreated soil, and 0% mortality after 28 days in soil after treatment. Seed germination tests resulted in 88-93% germination in treated soil after five days, compared to no germination at all for radish or oats and 30% germination of corn after five days in the untreated soil.
The bioreactor has potential as a natural process; it removes a large variety of VOCs, including high odor-removing efficiency; ease of operation and low maintenance; and wide applicability due to specific design flexibility.

The first project report (Budapest, 1992) presented general characteristics for the proposed biopile technology in a paper entitled “Biodegradation/Bioventing Process for the Treatment of Organic Contaminated Soil.” The second project report (Québec, 1993), entitled “On Site Remediation of Soil Contaminated with Transformer Oil and Diesel,” presented two case studies under extreme conditions (soil heavily contaminated with hydrocarbon and heavy clay soil). The current report focuses on air treatment at the end of the venting system.

During soil remediation, off-gases may contain VOCs ranging to hundreds of mg/m³. Traditional technologies include carbon adsorption, thermal or catalytic oxidation, and wet scrubbing. Biological treatment is an attractive alternative because of its low costs, inherent simplicity, and lack of secondary wastes. The system was field-tested with BTEX off-gases produced at a site where in situ bioventing and air sparging were used to remediate spilled gasoline.

The system consists of an air/water separator, trickling filter, and biofilter. The trickling filter housed a mixed culture of hydrocarbon-degrading bacteria sustained solely on the volatile hydrocarbons and supplemental inorganic nutrients (nitrogen and phosphorus). The trickle filter's irrigating water is continuously recirculated, and the gas is bubbled through in a countercurrent flow. The biofilter was a column filled with compost equipped with a gas-distribution system. Pollutants are adsorbed to the filter medium and degraded by indigenous microbes. No nutrient supplementation was needed for the biofilter due to high initial levels in the compost.

The system operated under winter conditions: though ambient temperatures fell below -21°C, temperatures in the trickling filter and biofilter were maintained at 25-40°C. Initial moisture content in the biofilter was about 60%. Since humidity control is critical in biofilters, occasional irrigation was used, despite the water-saturation of inlet gas, to offset the drying effect of the higher temperature due to exothermic reaction of pollutant biodegradation. The bacteria were isolated from gasoline contaminated soils, and consisted of five predominant strains. Counts of total colony forming units of heterotrophic bacteria did not vary greatly with time in either the trickling filter or the biofilter. However, the numbers of hydrocarbon-degrading bacteria increased by 3 to 4 orders of magnitude during biofilter operation and then declined as the hydrocarbon was used up.

Results over 127 days of operation showed BTEX removal of about 90%; with a residence time of less than 2 minutes the concentrations of these compounds were reduced to low or non-detectable levels. The system required a very short start-up period, with 85% BTEX removal reported during the first week. Provincial standards of 15 kg/day TOC is easily attained with the system. Future work will involve the optimization of system design and control of operating conditions to substantially improve the performance.
Soils from two former industrial sites exceeded guidelines for reuse due to heavy metals and PAHs. After treatment, all soils were brought to within residential or industrial standards. Recovered metals were suitable for off-site recycling in steel and base-metal industries, while recovered organic contaminants were low mass, highly enriched in product, and suitable for secondary treatment. The pilot-scale tests resulted in expected full-scale, cost-effective treatment of about 500 kT of heavy metal/PAH contaminated soils at one site and about 115 kT of lead-contaminated soil at another site.

The integrated treatment process potentially offers a number of economic and technical advantages over separate or sequential treatment of metals and organics, as well as utility over a wide range of contaminant and soil types. The approach uses gravity, physical, and hydrometallurgical procedures for metal recovery (leaching and chelation absorption of leached metals) and physical/chemical procedures for organics.

Four bulk samples of 35 T each from the Ataratiri site were mechanically blended and used for continuous treatment testing at a rate of 1 T/hr, which involved debris screening, wet scrubbing for fine particles, and gravity and magnetic separation processes for classification. Analysis of the samples revealed unacceptably high concentrations of Pb, Cu, Zn, Ni, Cd, As, Hg, oil/grease, and PAHs. Similar samples from the Longue Pointe site were contaminated with lead-smelter fly ash and by lead-acid battery recycling operations. No other organic or metal contamination was present at Longue Pointe.

Coarse and fine metals were recovered separately for iron-rich and base-metal-rich products, which enhanced recycling potential. All treated soils met requisite standards. Between 84-86% of the metal-contaminated soil mass was recovered for reuse. Physical/chemical recovery of water insoluble organic contaminants was reasonably effective. The bulk of the initial contaminants could be recovered to a concentrate of relatively low mass (2-7% of initial soil mass), highly enriched in oil/grease and PAHs. Recoveries in excess of 75% of oil/grease and 95% of PAHs were reported. Organic decontamination might be improved by washing with surfactants to remove and process surface organics; however, this was not tested. They currently are building a 600 tonne/day plant at the Longue Pointe lead battery site, which has concentrations of 3,000 mg/kg Pb; 80% of the Pb is adsorbed to clay surfaces.
At the 1993 conference in Québec City, the report described the bench- and initial pilot-scale experiments for constructing an on-site bioreactor to degrade PAHs. Experiments evaluated the addition of nutrients, bark and wood chips, compost, detergents, air, clean water, and increased temperature. Preliminary results reported last year show $10^5$-$10^7$ soil bacteria per gram, with potential to degrade phenanthrene, anthrathene, and pyrene.

The present report concentrated on laboratory tests designed to (1) estimate the number of natural PAH-degrading bacteria in the soil using $^{14}$C-marked PAH compounds and (2) discuss microcosm tests of these bacteria. Inoculation on agar plates, with PAHs, was unsatisfactory except for phenanthrene-degrading bacteria. Nevertheless, tests with radiolabelled PAHs confirmed that a population of PAH-degrading bacteria is present in adequate concentrations. Some success was reported by adding certain detergents to desorb PAHs from the soil into the aqueous phase and thereby increase bioaccessibility. Concentrations in the soil of PAH compounds were reported, ranging from <1 ppm for naphthalene to >20 ppm for flouranthene, with total PAH concentrations of about 400 ppm.

Phase II experiments were initiated using a column experiment to determine whether structural amendments like wood chips, compost, or aeration increases biodegradation, and a microcosm experiment to determine whether different temperatures ($15^\circ$C or $25^\circ$C) and addition of detergents increases biodegradation. The column experiment ran for 127 days, after which no significant change in PAH content in the soil was observed. The microcosm experiment ran for 325 days, during which there was no significant change in PAH content in the soil for the first four months, but when detergent was added, the PAH content was generally lower after time and there was a tendency for degradation. For the last 198 days, there was a degradation (microbial degradation or incorporation of PAHs in the organic fraction of the soil) on 66%-74% (for Phenanthren, flouranthen, anthracen, pyren, and benz(a)pyren). These results were the same for all treatments and for the control. It is believed that the absence of degradation during the first four months is due to an initial inhibition of the microorganisms, which is due to the addition of nutrient salts, resulting in high pH values in the soil.

Field testing of 10 homogenized plots (five outside and five inside) of 27-35 m$^3$ was initiated in June 1994. Monitoring of PAHs, dissolved gases, water, nutrients, and microbial activity will continue through October 1995. Results will be reported at the next conference.
Residues of cyanide and sulphate from a plant that converted coal gasification process wastes to MnSO₄ have contaminated the soil and groundwater. While MnSO₄ contamination is not common, cyanide residues are very common at such gasification sites. Traditional remediation (off-site incineration) was estimated to cost 8-13 million ECU, and there are about 125 gasification sites in Denmark. Consequently a pilot-scale demonstration was initiated to evaluate alternative remedial designs with a view to reducing costs.

Approximately 28 metric tons of cyanide and 1,140 tons of sulphate are the primary contaminants. Laboratory scale studies included the leachability of CN and SO₄ from the surface waste piles into the groundwater, the biodegradability of CN, and the possible treatment of leachate by flocculation or UV. At pilot scale, the project investigated the percolation of CN and SO₄ from the production wastes as a function of Eh and pH and the efficacy of treatment using membrane filtration and biodegradation. Both distillation of leachate and reverse osmosis also were considered, but rejected as economically infeasible when ultimate disposal of concentrated brines is considered. The SO₄ concentration in the vadose zone between leachate and groundwater was about 1,600 mg/L.

The surface wastes exhibited high leachability of CN and SO₄ especially at high pH (>10), and the leaching could be increased by adding NaOH to further increase pH. Since the pH of the groundwater is very low (3.4), and because cyanide will precipitate at low pH, relatively little cyanide is estimated to be in solution. The fine-particulate dust residue from the gas cleaning process could not be leach-tested at the pilot-plant scale. Experiments to precipitate SO₄ with BaCl₂ worked, but left unacceptable Ba and Cl levels as residues. Also, full-scale barium treatment would have required an estimated 400-620 tons/year of BaCl₂ a prohibitive expense. Pilot-scale biological treatment was unproven due to the unreliability of the system over time. The costs associated with full-scale biological treatment, including expensive and labor-intensive monitoring, did not permit further investigation.

In situ treatment was practical only if SO₄ leaching was artificially accelerated, and then only in frost-free seasons. Infiltration of neutral water would preserve groundwater conditions, but would take too long. Infiltration by NaOH would accelerate SO₄ leaching, but would precipitate iron hydroxides and otherwise add a chemical agent to the groundwater. Ex situ (batch) treatment is estimated to take 18 years, an unrealistic timeframe. In situ treatment of the cyanide proved infeasible during the pilot tests due to unacceptable clogging. In situ biological treatment is predicted to take 7-10 years at pilot scale, still leaving an unacceptable residue of cyanide.

In conclusion, ex situ treatment of the SO₄ production waste is infeasible due to high costs, long duration, and redisposal of effluent. In situ treatment is infeasible due to effluent disposal problems. The scale-up from pilot to full-scale will require significant and costly modification, as well as considerable labor to maintain the system. The unusual pH conditions at the site, together with
the conflicting responses of SO₄ and cyanide to pH changes, make the problem economically intractable. The results of the pilot test seem to recommend leaving the MnSO₄ wastes on site, covered with clean soil from other locations, together with regular groundwater monitoring. No treatment will be contemplated as long as the SO₄ concentration remains below 250 mg/L. Solute transport modeling confirmed that the SO₄ plume is not likely to expand. The 800 tons of cyanide-contaminated waste will be excavated and incinerated.

<table>
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<th>Project Title</th>
<th>Ozone Treatment of Contaminated Groundwater</th>
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<tr>
<td>Location</td>
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<tr>
<td>Project Status</td>
<td>Final Report</td>
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<td>Contaminants</td>
<td>Chlorinated solvents, esters, phenols, and aromatic hydrocarbons</td>
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<td>Technology Type</td>
<td>O₂/UV degradation after Biological pretreatment</td>
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Biological pretreatment degrades contaminants into forms that can be treated more effectively by photochemical oxidation, thus optimizing the cost and performance of the remediation.

From 1963 to 1972 indeterminate chemical wastes were dumped into an abandoned limestone quarry. In 1980, contaminated groundwater and resulting bad odors were noticed from water percolating out of a natural seep at the base of a 20 m limestone hill down-gradient from the quarry, near the Autumn River valley. Under the limestone is a layer of fine sand underlain by a thick impermeable clay. The sand layer is a drinking water aquifer. The contamination plume has penetrated the limestone and sand to a depth of 40 m beneath the quarry. Clean up was initiated in 1991 when the French Energy and Environment Agency assumed responsibility for the project. The annual flow of the 20m-thick contaminated plume is estimated to be 50-80,000 m³, or 25 m³/hr. Over 20 toxic chemicals were identified in the groundwater, including chlorinated and nonchlorinated solvents, alcohols, petroleum hydrocarbons, aliphatics and aromatics, and volatiles. Ethanol, phenols, chlorinated solvents, BTEX, acetone, and several aliphatic hydrocarbons were noted in concentrations exceeding milligrams per liter. Chemical oxygen demand was 250 mg/l; total organic carbon was 60 mg/l; and AOX was 5.5 mg/l.

A 600 m long, 6 m deep drainage trench was constructed at the base of the cliff to intercept the groundwater flow. Contaminated water was pumped to an aeration reactor, where organics were microbially degraded. Activated sludge was separated from the treated water using a membrane filter, resulting in 5 times greater biomass retention and 5 times lower sludge production. Concentrated chlorinated aliphatic and aromatic contaminants are then oxidized to the point where they can be naturally biodegraded.

During the pilot testing, experiments were conducted with and without biological pretreatment, and with oxidation with ozone, peroxide, and UV in various combinations. After pretreatment and ozonation, significant reduction in chlorinated hydrocarbons below detection limits was reported. Concentrations of COD were 239 ppm in the raw water, reducing to 28 ppm with ozonation alone, and undetectable after pretreatment and ozonation. Dissolved constituents were reduced by 80-85%, and 100% of VOCs were eliminated. Estimated costs for reducing VOCs to acceptable drinking water limits were FF15 million (capital cost) plus FF23.7 million annually. Meeting acceptable surface water discharge levels would cost about FF10 million initially, with an annual cost of FF1.7 million. Ozone consumption was higher in an O₂/H₂O₂ system than in O₂/UV, but the results were the same.
Dump sites of former coal tar and petroleum distillation plants in France are characterized by high concentrations of total hydrocarbons (2200 mg/kg in soil and 4800 mg/kg in settling ponds), phenols (3 and 10 mg/kg), PAHs (1500 and 850 mg/kg), and cyanides (10 and 300 mg/kg). The cyanides are bound to the sediment. Research was conducted to identify PAH-degrading bacteria, evaluating PAH bioremediation practicability, and evaluating whether oxidizing pretreatment will increase bioremediation of PAHs.

Five fungi and nine bacteria were tested on PAHs in a recirculating water bioreactor. The test piles were constantly mixed and aerated. Amendments of straw (50-100 kg/ton), sawdust (20-50 kg/ton for sludges only), and 50% clean soil (for sludge only) were evaluated. Inorganic nutrients were provided in 2-5 kg/ton of Max Bac, a proprietary timed-release nutrient claimed to be specially formulated to speed the microbial degradation of hydrocarbons. Four bacteria but no fungi showed PAH degradation after a 2 month trial. During the pilot testing, it became apparent that the high tar concentrations in the soil made it difficult to get full mixing and therefore limited bioaccessibility. Similarly, it was speculated that heavy clay soils might inhibit the process unless the piles could be thoroughly mixed. Nevertheless, PAH degradation of 75% (800 ppm to 200 ppm) was achieved in 12 months, during which time total hydrocarbons were reduced from 1,275 ppm to about 220 ppm. Phenols were quickly degraded (within 7 weeks they were reduced by 75%), while cyanides were much slower (2-3 months for 50% destruction). Three oxidizing pretreatments were tested by mixing them in as the on-site piles were constructed: hydrogen peroxide, sodium hypochlorite, and ozone.

In summary, biological seeding was necessary after initial sterilization; the rate of oxidation must be high in order to see positive results with PAHs; bioremediation rate is increased with oxidation; and an oxidizing catalyst such as ferrous sulphide reduces the amount of nutrients necessary. In 19 weeks, 1000 ppm PAHs was reduced to 50 ppm with pretreatment, hydrogen peroxide, and a ferrous sulphide catalyst.
Below a former gasworks site in Karlsruhe, PAH contamination of a gravel/sand aquifer extends to a depth of 10 m, with the zone of maximum contamination lying between 5 and 7 m. In this zone 14,000 mg/kg of PAHs have been detected in the <2 mm fine soil fraction. The contaminated area was sealed with walls extending 17 m into an impervious clay underlayer. The water table in the confined zone was lowered, and an air venting system installed; the horizontal permeability exceeded the vertical permeability. Oxygenation of the pore water was continuous from the injected air, and continuous irrigation from the surface provided moisture and inorganic nutrients to the microorganisms. Flushing water was warmed and enriched with nutrients. Periodically, the soil was flushed with large volumes of water to measure the remaining concentration of contaminants and soil gases.

Core sampling was conducted to determine the degree of contamination. Samples of 16 PAHs and 2 methylnaphthalenes were evaluated gravimetrically, by infrared spectroscopy, and by gas chromatography. Apart from the unevenness of contaminant distribution, chemical quantification was highly dependent upon the method of analysis. Gravimetric determination of lipophilic organics resulted in total contamination of 5,000 kg, IR measurements showed only 2,000 kg, while GC analysis of total PAHs was 600 kg. Lipophilic organics turned out to be the most suitable parameter to quantify the total contaminant load.

Unfortunately, engineering difficulties and the natural heterogeneity of the substrate made it impossible to extract meaningful samples from reboring the original cores. Consequently, the biodegradation process was monitored after a year by extracting frozen, undisturbed cores from within the treated areas as well as from the surrounding (contaminated but untreated) areas. Since the composition of PAH is nearly constant, heavy PAHs (>4 rings) can be used to measure degradation because this fraction is in nearly constant proportion to the original total contaminant load. Monitoring produced a relative increase in PAHs that indicated a degradation of 54% in highly contaminated samples. Laboratory experiments with undisturbed soil samples showed significantly higher degradation. Depending upon the kind of measurement used, two years of biodegradation showed 70-90% destruction of PAHs. Monitoring of CO$_2$ and O$_2$ over three years enabled a calculation of the soil respiration rate, which is a measure of the biological degradation rate. The data showed that 7,700 kg of O$_2$ were consumed and 7,600 kg of CO$_2$ were produced, indicating decomposition of about 2,400 kg of organic material. Soil aeration and nutrient addition greatly increased degradation rates. The large O$_2$ demand demonstrates the necessity of lowering the water table for aeration by venting.

The extreme heterogeneity of the subsoil greatly complicated the determination of bioremediation efficiency. The main limiting factor seemed to be the contaminant bioavailability in the aquifer. During the three-year project, chemical oxygen demand decreased by 83%, dissolved organic carbon decreased by 76%, and the overall decrease of PAHs in the flushing water concentration was 97%. The bioluminescence test for toxicity indicated 98% detoxification. Overall, about 54% of the soil PAHs was degraded after 2½ years. Thus, while a lot of PAHs remained in the soil, its toxicity was considerably reduced.
This project demonstrated the first full-scale application of vacuum distillation technology, which is proven effective for soils contaminated with volatile and semi-volatile substances like tar fractions, oil, and mercury. The technology can be used in conjunction with soil washing for soils or fractions with high silt/clay concentrations or with very high contaminant loads. In this application, mercury-contaminated soils excavated from a former chemical plant were successfully reduced from peaks of 1900 mg/kg to below the target level of 50 mg/kg, frequently reaching 20 mg/kg. So far, 15,000 tons of contaminated soil have been treated successfully, with an average throughput of 150 tons/day.

Soil washing is used to produce a concentrated fraction in the size between 100 µm and 8 mm, and then vacuum distillation removes the contaminants. Precipitation sludge is disposed separately, and used ion-exchange resin is recycled off-site. Thermal desorption at 100°C is followed by a vacuum distillation process in which the soil is heated in a rotating drum to 350-450°C under reduced pressure (50-150 hPa). Mercury is volatilized and recovered by recondensation. The use of reduced pressure (rather than higher temperatures) permits significantly lower energy costs and only 1/20 to 1/30 of the flow of process treatment gas that is considered normal for incineration. Since vacuum distillation permits a low O₂ environment, secondary oxidation does not occur and dangerous organic residues like dioxin cannot be formed. Treated soil with residual concentrations still greater than 50 mg/kg are passed again through the treatment process.

Soil exiting the dryer has a residual moisture content of under 1%. Off-gas from the drying step is treated in a vent condenser. Treated soil is remixed with coarse materials and disposed of in a landfill. Tests have proven that, in addition to mercury, volatile and semi-volatile contaminants such as BTEX, solvents, TPHs, PAHs, and phenols can be successfully treated.
Following the final pullout of former Soviet armies from Hungary in 1990, the Hungarian Ministry for Environment conducted an environmental assessment and damage survey following a method acceptable to both the Hungarian and Soviet governments. There were 171 garrisons, 340 settlements, 6,000 major buildings, and 46,000 ha of land in the survey. Forty percent of the damage comprises soil and groundwater contaminated with hydrocarbons and heavy metals. The most polluted are six military airfields contaminated with jet fuels and fuel oils. Because of time and funding constraints, work was begun in 1991 at the 20 most-polluted bases, with an objective to contain the pollution. By the end of 1993, full remediation was accomplished at 8 sites, while the remaining 12 major sites were completed in 1994. The goals of the 1993-94 assessment was to identify those remaining sites that require remediation and determine those sites where only monitoring is necessary.

Tököl airbase was one of the principal sites that needed prompt remediation. Located just 600 m from the Danube River, it overlies an aquifer supplying about 5% of the municipal water for Hasztelek. The water table is 4 to 5 m, and the aquifer is a Pleistocene sand/gravel layer 10 to 15 m thick, underlain by impermeable clay. Contamination from the airfield is migrating towards the Hasztelek wellfields and will reach it within 20 years.

Remediation at Tököl was accomplished in phases between August 1991 and June 1993. Free product was separated from contaminated groundwater by depressing the water table to speed flow of groundwater to extraction wells, pumping, and on-site water/oil separation.

Recovered free product amounting to 224,000 liters and about 700,000 liters of jet fuel were recovered from 279,000 m³ of pumped groundwater. Remediation at Tököl was accomplished in cooperation with the Danish Agency of Environmental Protection. A technical report by the Danish EPA is also available (see page 48).
A wetland is receiving dense non-aqueous-phase liquids (DNAPLs) from a nearby abandoned wood-treatment plant. No human health risk exists, only ecological. The objective of this project was to evaluate soil washing of creosote-contaminated soil followed by bioslurry treatment of the PAH-containing sludge at pilot scale. The pilot plant included a 1 tonne/hr washing plant and a 454 liter bioslurry reactor. Soils from the site were screened to <2 cm because particle size distribution is very important to soil washing effectiveness. Six different soils were tested, comprising sand, silt, clay, and sawdust/sand. Water temperature, pH, foammers, and surfactants were evaluated. A companion composting test did not work well due to clumping because of high clay content.

Soil washing results indicated that cationic collectors combined with a foamer were most effective, exhibiting 90-95% PAH removal from sandy soils and 20-90% removal from clay soils. Raising water temperature or pH had no significant effect.

The technical feasibility of soil washing was proven at pilot scale, resulting in up to 97% PAH removal and 40-50% volume reduction. The slurry biotreatment used indigenous microbacteria populations and inorganic nutrient amendments and was reported to be 98% effective after 8 days. A Microtox 15-minute bioassay showed a 10-fold decrease in toxicity after treatment.

Three areas exhibited PAH concentrations above 200 mg/kg. Treatment options at full scale include in situ impregnation, excavation and ex situ biotreatment sediments, excavation of landfill soils followed by soil washing/biotreatment, and just monitoring. Full excavation and treatment will involve 25,000 m³ and would cost about US$6.3 million. In situ biotreatment and limited excavation would entail 8,000 m³ at a cost of US$3.5 million, and covering and monitoring at two separate sites would cost about US$1 million.

Process costs for excavation, sorting, and backfilling were demonstrated at about US$160/m³, washing at US$300/m³, biological treatment at US$260/m³, and pumping-and-treating at about US$530/m³ (although the pump-and-treat estimate is more uncertain since it includes the removal of the free phase and air injection to increase pumping rates).
The goal of this project is to investigate the applicability of simplified and mechanistic models used during soil remediation. The mechanistic model being used by the project is the ECOSTAT model, a chemical equilibrium model that is being modified for bioventing. In order to study the applicability of this model, the project compares prior predictions of the remediation efficiency with results obtained in full-scale soil venting remediations.

In order to design and evaluate *in situ* soil remediation techniques, tools are needed for modeling subsurface physical, chemical, and biological processes. However, available information for conducting soil investigations is limited, and only rough estimates of remediation timeframes, based on average value, chemical equilibrium, and first- or zero-order of decay, can be made.

Decreasing soil contaminant concentrations are often predicted using geohydrological flow patterns in the subsurface. In practice, however, these predictions are found to be too optimistic. For example, after a rapid contaminant concentration decrease, the rate of remediation slows down and eventually stagnates, resulting in a remediation timeframe that often is longer than originally predicted. Sometimes this difference is small and can be accounted for using uncertainty factors; other times, the difference is large, resulting in a much longer soil remediation timeframe. Stagnation implies that some fraction of contaminants is not available for leaching, volatilization, or biodegradation. A number of factors may contribute to this, including non-linear sorption, non-equilibrium kinetics, or spatial variability in hydrology or chemistry.

The objective of this project is to develop a process that combines *in situ* remediation experience with the fundamental knowledge of chemical and biochemical processes in order to develop a process to more effectively determine soil remediation time frames. Predictions can be considerably improved using detailed soil mapping processes and conducting experiments with the contaminated soil. However, these processes can be very time-consuming and expensive. As an alternative, this project proposes developing a “tailor made” site-specific soil investigation strategy that is able to identify the parameters that determine most of the uncertainty in the prediction. This project focuses primarily on the investigation and description of non-equilibrium phenomenon observed by full-scale vapor extractions and remediations.
Promising results were reported for the elimination of mineral oil and PAHs using the combined washing/UV-H$_2$O$_2$ pretreatment/bioslurry process. However, the process requires further refinement for persistent xenobiotics. Success with the combined process requires detailed characterization of the contaminant distribution and soil, but allows customized remedial designs to take advantage of the positive aspects of the component techniques.

Hydraulic (hydrocyclone) separation, photochemical treatment, and bioremediation each exhibit strengths and weaknesses. The goal of this demonstration is to combine the separate technologies into a treatment train to take advantage of the strengths of each. Hydrocyclone separation is used to concentrate specific contaminants in selected soil fractions, UV/H$_2$O$_2$ pretreatment is used to transform non-biodegradable contaminants into biodegradable fragments (rather than to break down persistent organics), and bioremediation is used for the final destruction of organic compounds or residues. The goal is to produce clean soil, with no toxic residue, in a reduced time. The combined remediation process is called “Fast Organic Removal Technology,” or “Fortec”.

Testing was done with UV/H$_2$O$_2$ pretreatment followed by biodegradation of mineral oil and PAHs. Biodegradation of mineral oil was very fast (5,000 ppm mineral oil was reduced to <100 ppm in 3 to 8 days). There was no significant effect of photochemical treatment, as it was masked by the high initial biodegradation rate. No significant volatilization occurred during aeration. PAHs had a relatively short treatment period (30 ppm reduced to 2-4 ppm in 15 days). UV/H$_2$O$_2$ pretreatment was indispensable, however, for the recalcitrant PAHs. The PAH availability to the UV/H$_2$O$_2$ pretreatment appeared to be the rate-limiting factor. However, poor mass balances were obtained for PAHs, indicating the technique needs further refinement. A laboratory trial with the pesticide β-hexafluorohexane (Lindane) did not show any degradation, its chemical stability apparently too high for photochemical breakdown.

Because high-molecular-weight PAHs exhibit slow biodegradation, further slowed by limited bioavailability due to adsorption to soil organics, an experiment was tried to increase bioavailability by UV/H$_2$O$_2$ destruction of the organic matrix. The experiment was successful, with the pretreated sample exhibiting 63% destruction, compared to 23% destruction of non-pretreated PAHs over 12 days. A full-scale demonstration plant will be constructed for further pilot testing.
<table>
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<tr>
<th>Project Title</th>
<th>Sorption/Solidification of Selected Heavy Metals and Radionuclides from Water</th>
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<tr>
<td>Location</td>
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| Country Representative | Reşat Apak  
Istanbul University  
Istanbul, Turkey  
tel: 90/1-5911-996  
fax: 90/1-5911-997 |
| Project Dates | N/A                                                                             |
| Media         | Water                                                                           |
| Costs Documented? | No  
Project Size  
Bench scale  
Report Available?  
Yes |

Laboratory experiments were designed to test the removal of heavy metals (Hg, Cd, Cu, Pb) and radionuclides ($^{137}$Cs and $^{90}$Sr) from water by stabilizing them in bauxite wastes and coal fly ashes acting as adsorbents to prevent leaching. Adsorbents were red muds from aluminum plants containing mineral oxides of aluminum, silicate, and iron; and coal fly ash containing oxides of aluminum, calcium, silica, iron, potassium, sodium, and magnesium. Both materials were strongly alkaline when leached with water, so they were first washed with weak warm HCl and baked dry. Washing removed about 40% of the initial fly ash by weight. Reducing the alkalinity of the red muds and fly ash was important to meet U.S. EPA alkalinity regulations.

Various concentrations of metal ions were tested with the adsorbents in various raw and treated forms. Stability was tested by desorption attempts at low pH (4.5) in CO$_2$-saturated solutions and in neutral buffered NaHCO$_3$. Batch adsorption experiments resulted in very high values of absorption (>99.9%), and the experiments will be retried using higher metal ratios. The order of adsorption efficiency for the metals was Hg >> Cu > Cd > Pb. Since all tests showed only a few percent leaching efficiencies, the adsorption was essentially irreversible, even in changing aqueous conditions of pH and ionic strengths. Although the radionuclides were relatively insensitive to acid pre-treatment of the adsorbents, combined acid and heat treatment was beneficial for $^{137}$Cs adsorption and detrimental for $^{90}$Sr adsorption, probably due to the change of sorption made after this treatment.

Desorption coefficients for the radionuclides exhibited significant differences than for their adsorption coefficients, possibly due to irreversible fixation during adsorption. However, data were reported showing radionuclide desorption of only a few percent, at most. $^{90}$Sr adsorption is exothermic and essentially irreversible, and both the fly ash and red muds exhibited strong affinities. Both $^{137}$Ce and $^{90}$Sr adsorption are affected by inert electrolytes. Radiostrontium adsorption generally increases with pH, while radioesium adsorption is maximal around the neutral region.

While stabilization tests were conducted on the fly ash and red muds as well as on the adsorbents after they were loaded with contaminating metals, only the results of the unloaded materials were reported. Solidification was accomplished in prepared cement, standard sand, and carefully measured water. Red muds and fly ash were added to the cement mixture. In concentrations below 20%, the compressive and shear strengths of the doped concrete were not significantly different from the control concrete. However, there is a critical weight percentage of 10-20% additives above which the strength declines dramatically.
The application of traditional solidification/stabilization techniques such as cementitious and pozzolanic materials, for the treatment of soils polluted with organic contaminants, has been limited by reported detrimental effects on cement hydration, structural formation, and contaminant stabilization. The technology under development, an advanced stabilization/solidification process, aims to overcome these limitations for the treatment of soils contaminated with stable and recalcitrant organic waste materials.

The process is based on the use of modified organophillic clays with specially intercalated additives. Commercial organoclayes are typically quaternary ammonium salt substituted clays e.g. montmorillonite. Such minerals possess a combination of cation exchange, intercalation and swelling properties which make them unique. Pillared clays have been developed with the ability to withstand excessive dehydration without loss of stability. The intercalated “pillars” act as molecular props creating a two-dimensional porous interlayer structure which allows larger organic molecules such as PAHs to be accommodated. Examples of pillaring agents include transition metal complexes, heteropoly acids/polymer and organometallic cations. Clays substituted with metallic cations such as Fe³⁺, Al³⁺, and Cu²⁺ create a variety of reactive sites for the chemical fixation of organic contaminants. By selective use of clays and intercalation of appropriate quaternary ammonium ions with relatively low cost pillaring agents and reactants (principally Fe/Al compounds), a highly efficient and multifunctional treatment media may be produced which can be applied on a cost-effective basis.

Once the clay is added to the contaminated soil, the reactive properties of the clay will ensure that organic contaminants are chemically bound to the clay matrix. The immobilized contaminated clay can then be solidified by conventional cement hydration techniques using a mixture of Ordinary Portland Cement and pozzolan. An important consideration of the stabilization/solidification process is to ensure a homogeneous mix of the contaminated soil and chemical additives. The application of the technology as both an *in situ* and an *ex situ* process is being investigated within the research program.

The first phase of the project is supported by the U.K. Department of the Environment through the U.K. Government's Environmental Technology Innovation Scheme (ETIS). The technology evaluation program will comprise a series of chemical leachability and physical property/permeability testing procedures. Special instrumentation techniques including Fourier Transform Infra Red (FTIR) will be used to demonstrate chemical bonding of specified organics to the clay matrix and/or the reactive clay pillar structures. A full-scale trial will be carried out in the second phase of the project.
Laboratory scale studies of mineral processing techniques were conducted on lead and zinc contaminated spoils from abandoned mines in mid and north Wales. These techniques, used to extract metal-rich ores from less valuable waste material, may be applicable to the removal of contaminants from metalliferous spoil materials to reduce the environmental impact of such spoil. The evaluation of techniques represented the first phase of a two-part study to identify the promising treatment options for a detailed examination in the second phase of the study.

Characterization of the mine spoil was carried out to determine the mineralogy of contaminating particles and the distribution of contamination according to particle size. Concentrations of lead and zinc in the whole spoil samples were up to 20% and 15% by weight respectively. Lead was observed to concentrate in the finer particle sizes of the spoil. Weathered spoil samples contained a much higher content of oxide, carbonate, and sulphate mineralogy than fresh spoil samples which contained sulphide.

Mineral processing techniques exploit physical and chemical differences between contaminated and uncontaminated particles. Differences in particle density and surface chemistry for the separation of spoil particles were evaluated using dense media (so called “sink and float”) and froth flotation tests. A Multi-Gravity Separator (MGS) was used to further evaluate density separation at pilot scale. Laboratory-based density separation resulted in consistently reduced metal concentrations (<2% by weight) in the lighter spoil fractions representing over 90% of the total sample weight. The heavier concentrate contained up to 32% lead and 5% zinc by weight. Although significantly cleaner than original spoil these levels still greatly exceeded U.K. soil guidelines. The pilot scale MGS treatment produced similar results on the <0.5 mm fraction of spoil. The effectiveness of the froth flotation trials depended critically upon the mineralogy of the spoil. Unweathered material, rich in sulfides, resulted in better segregation of contaminants into the concentrate.

Leaching of metal contaminants from the spoil by a variety of chemical agents such as sulfuric acid, sodium hydroxide, diethylenetriamine, and by using ferric bacteria inoculum, was evaluated on unprocessed spoil and treated fractions from the density and froth flotation tests. Effective chemical leaching depended on the degree of spoil weathering. Sodium hydroxide leaching of weathered spoil mobilized between 25 and 92% of the lead and between 3 and 23% of the zinc in unprocessed spoil. Generally, sulfuric acid and diethylenetriamine leached between 2 and 33% of the lead, and between 12 and 64% of the zinc. For previously treated spoil leaching of between 2 and 5% of the contaminants was observed indicating a resistance to leaching in residual material. Bacterial leaching of lead proved to be ineffective but significant movement of zinc from the spoil was recorded.

It was recommended that future work focus on the applicability of alkaline leaching and its integration with gravity separation methods for the treatment of this type of metalliferous waste. Further work on the pilot scale assessment and optimization of the MGS was also suggested.
<table>
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<tr>
<th>Project Title</th>
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<td>Location</td>
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<td>Technical Contact</td>
<td>Ken W. Brierley</td>
</tr>
<tr>
<td></td>
<td>British Nuclear Fuels plc</td>
</tr>
<tr>
<td></td>
<td>Warrington, United Kingdom</td>
</tr>
<tr>
<td></td>
<td>tel: 44/925-834-656</td>
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<td>Pilot scale</td>
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CACITOX™ is a multi-component leaching process using a proprietary combination of highly selective and environmentally tolerant reagents. The CACITOX™ reagent comprises low concentrations of carbonate, oxidants, and complexing agents, which convert insoluble or absorbed contaminants into soluble complexes. The oxidant dissolves certain metals found in their less soluble forms. The low reagent concentrations and its high selectivity result in minimal secondary waste. CACITOX™ is distinguished from conventional soil washing by its ability to selectively leach the contaminants from soil as soluble chemical complexes.

The project consisted of three phases: evaluation of the process with heavy metals; evaluation with radionuclides; and engineering design for mobile ex situ soil treatment plant. Early testing demonstrated the effectiveness of the CACITOX™ process in reducing contaminant concentrations to regulatory levels, even with high-clay soils. There are four stages to the process: (1) size classification, where oversize materials are sorted out and contaminated soil volume is reduced by concentration; (2) soil leaching using the CACITOX™ reagent, with laboratory-optimized parameters for the particular soil/contaminant conditions of the site; (3) soil/leachate separation using a bank of hydrocyclones, followed by dewatering with filters; and (4) leachate treatment using precipitation and ion exchange processes. Precipitated contaminants are ultimately treated by containerization, encapsulation, or dewatering. The pilot-scale transportable plant has a capacity of 10 kg/hr, with easy scale-up to 100 kg/hr.

Performance evaluation was accomplished at bench scale using synthetic test soils spiked with aqueous solutions of the nitrate form of commonly encountered metals. Seven heavy metals and six radionuclides were evaluated at “low” and “high” concentrations. Since clay soils proved the most intractable, most testing occurred with fine-particle soils. In general, all heavy metals partitioned in a similar manner in the various soil size fractions. While the clay and silt fractions contained the bulk of the spiked contamination, 26% of the contaminants were contained within the coarse sand/gravel fractions. For the “high” spiked samples, the coarse fraction failed to meet the Dutch “B” Values or Canadian Residential levels. Thus, conventional soil washing alone, which relies on particle size classification, would be ineffective in treating these soils. Soil pH did not appear to significantly affect contaminant removal. While the process failed to meet regulatory levels for Cd or As spiked with 1000 ppm, it was reported that further optimization of the reagent formulation would enable target values to be achieved. Similarly, the addition of organic contaminants had little effect on initial leaching efficiencies, and 98% of the organics were removed from the soil. Removal efficiencies were comparable to leaching with mineral acids, but CACITOX™ dissolved less than 10% of the soil matrix (compared to 40% for acid washing).

Results also demonstrated that significant decontamination of radionuclide-contaminated soils occurred after a single contact with CACITOX™, and further improvement in radionuclide removal efficiency was predicted. Only Cs proved intractable, probably due to its monovalent state and ion size.
In-pulp adsorption technology was originally developed for the extraction of uranium from ore and extracting gold from matrix. In this technology, active carbon or cation exchange resins are mixed directly with the contaminated soil slurry. It is preferable to conventional chemical leaching for finer particle sizes (silt and clay). Contaminated substances may then be desorbed from the recovered carbon or ion exchange resin, which is then recycled. The system reported here also includes *ex situ* soil washing and chemical extraction using acid or alkaline agents. If the soil is sandy then filtration and washing is feasible, followed by precipitation or adsorption of contaminants from solution. However, if the soil is high in clay, then washing is less practical and in-pulp adsorption is more attractive. Current gold-recovery plants are operating at 1.2 million tons/year, which seems a reasonable size for contaminated soil remediation plants. Laboratory data were used to design equipment for a pilot-scale plant (3,000 tons/day), and a financial model constructed for the site showed that the treatment cost would be £70-80/ton. However, the pilot plant was not built.

Soil quantification is a critical step, as it may not be possible to achieve low absolute standards required for some metals such as arsenic. In these cases, pretreatment such as flotation or size separation and leaching may be necessary, and the in-pulp process may be complimentary to other processes. The leach is necessary to render some contaminants in a form suitable for adsorption. Various adsorption resins (strong and weak, cationic and anionic, chelating) were tested together with activated carbon and magnetite. Ion exchange resins were preferred for Cu, Cr, and Zn, but As removal has proved difficult, because at the very low pH (<1) necessary to dissolve the element and avoid iron precipitation, arsenic acid is not dissociated and therefore will not undergo ion exchange. Sulfuric acid was the most effective leaching agent, removing 90-97% of the contaminants at the test site. Copper, zinc, and chromium metals were removed to below target levels, but As exceeded the target. Chelating reagents were able to remove only 52% of As, and a combination of flotation, screening, and hydrocycloning achieved only 60% removal in 80% of the soil, but still above regulatory standards. Multiple acid leaching was able to reduce As from 650 to 22 ppm (within regulatory levels), but at a relatively high cost.

Mercury contaminated soil was leach-tested with various acids and at various temperatures. Hg adsorption is slow, elution is difficult, and the target of 0.5 ppm was very difficult to reach. High temperatures (550°C) achieved better results, but did not achieve regulatory levels. Achieving low absolute levels can prove difficult and costly, while a leachability criterion is easier to meet.

A sample of harbor sediment heavily contaminated with organics and metals was tested with various acids. Nitric and hydrochloric acids were successful, but sulfuric acid did not remove the lead. Because a substantial amount of calcium was also dissolved, and would interfere with ion exchange of the contaminants, a two-stage leach was developed. There was no observable effect by the organics on the leaching, and the organic removal could precede or follow metal removal.
Physical separation techniques can be used to divide contaminated soil into fractions that can be relatively easily treated. Physical treatment can also act as an early process in a treatment train involving chemical, biological, or thermal processes to reduce the volume of material requiring subsequent remediation and to convert the material into a more suitable form (such as a slurry). Although physical treatment alone could not reduce the absolute concentration of heavy metals to acceptable levels in some soils, physical treatment in combination with a mild acid leach was reported to reduce mobile contaminants in soil to below a leachability criterion. The reported soil washing included physical particle separation and chemical extraction using acids, alkalis, surfactants, and complexing agents.

A number of 5-20 kg samples of contaminated soil were collected from various representative locations throughout the U.K. for bench-scale characterization testing. Sites included former gasworks, coke works, canal dredgings, chemical works, metal reprocessing and pickling plants, and chromium- and mercury-contaminated sites. Contaminants included arsenic, complexed cyanides, mercury, chromium, copper, lead, nickel, zinc, PAHs, and petroleum hydrocarbons. Twenty to fifty tons of soil from the metal reprocessing works and gasworks were additionally sampled for pilot-scale testing.

Bench-scale analyses involved grain-size distribution and fractioning, hydrocyclone and attrition scrubbing with various reagents, specific-gravity tests of preferential contaminant partitioning, froth flotation testing of contaminant hydrophobicity, and magnetic susceptibility tests to determine preferential contaminant partitioning based on magnetic properties. Froth flotation is suited to fine grain sizes but an excessive clay content interferes with flotation performance by shielding particle surfaces from collector attachment. Therefore, in this project tests were generally conducted by desliming the sample (removing <10µm particles) before flotation.

Clay fractions showed higher contamination than the coarser fractions. Lengthening the time of attrition scrubbing did not appreciably remove contaminants, which is thought to result from the adsorption of contaminants within the pores and thus not accessible to surface abrasion. Heavy metals were present in all fractions with a specific gravity (sg) greater than 2.8, and the greatest weight percentage of contaminants exists in the <2.5 sg fraction. The soil from the metal reprocessing plant showed that 91.7% of the sample weight was associated with the <2.99 sg fraction, and the TCLP result was 15 times lower than the criteria for Pb, 54 times lower than for Zn, and 59 times lower than for Cu. A potential treatment process for this soil was therefore reported as a combination of physical separation as a pretreatment for fines and concentration of a substantial quantity of the heavy metals by gravity. This low volume concentrate and the fines would be stabilized, while the remaining bulk could be acid-leached to remove mobile species. Froth flotation studies on the fine fraction demonstrated a 53% reduction in petroleum hydrocarbons and 45% reduction in PAHs. When applied to the <3 mm fraction from the former coke works, the technique resulted in significant concentration of PAHs, mineral oils, and heavy metals. Ninety six percent of the mineral oils and 80% of the PAHs could be removed in froth concentrates, which constituted 32% of the original contaminants. Heavy metals recovery ranged from 50-70%. Froth flotation gave a poor response in metals removal to the metal-
reprocessing and chemical works soils. Magnetic separation investigations implied that commercial exploitation of this technique may not be cost-effective.
The technology was demonstrated under the SITE program for the treatment of groundwater contaminated with volatile organic compounds (VOC) including trichloroethane (TCE), tetrachloroethene (PCE), 1,1,1-trichloroethane (TCA); 1,1-dichloroethane (DCA), and chloroform. Trichloroethane and PCE were the principal contaminants with concentrations of about 1,000 and 100 µg/L, respectively.

The perox-pure™ system generally produced an effluent that contained TCE, PCE, and DCA at levels below detection limits, and TCA and chloroform at levels slightly above detection limits. The system achieved maximum removal efficiencies of greater than 99.9, 98.7, and 95.8 percent for TCE, PCE, and DCA, respectively. The system also achieved removal efficiencies of up to 92.9 and 93.6 percent for TCA and chloroform, respectively. GC-MS analysis of the influent and effluent samples for VOCs indicated that no new target compounds or tentatively identified compounds (TIC) were not formed during treatment. However, the toxicity of the effluent to water flea and flathead minnow was found to be greater than for the influent probably due to residual hydrogen peroxide being present. The treated effluent met California drinking water action levels and Federal drinking water maximum contaminant levels for all VOCs at the 95 percent confidence level. Cost analysis indicated that the groundwater remediation cost for a 50 gallon per minute perox-pure™ system would range from $7 to $11 per 1,000 gallons, depending on contaminated groundwater characteristics. Of this total cost, the perox-pure™ system direct treatment cost would range from $3 to $5 per 1,000 gallons.

The perox-pure™ system uses UV radiation and hydrogen peroxide to oxidize dissolved organic compounds present in water at parts per million levels or less. The goal is to oxidize organic compounds to carbon dioxide, water, chlorides, or possibly simple organic acids. UV is generated by 5 kW medium pressure mercury vapor lamps. These lamps are fitted with wipers to remove an organic coating that tends to build up during operation and may reduce their efficiency. This treatment technology produces no air emissions and generates no sludge or spent media that requires further processing, handling or disposal. Ideally, end products include water, carbon dioxide, halides, and in some cases, organic acids. The principal oxidants in the system, hydroxyl radicals, are produced by direct photolysis of hydrogen peroxide at UV wavelengths.

The perox-pure™ chemical oxidation treatment system used for the SITE technology demonstration was assembled from the following portable, skid mounted components: an oxidation unit, a hydrogen peroxide feed module, an acid feed module, a base feed module, a UV lamp drive, and a control panel. The oxidation unit has six reactors in series, with one 5 kW UV lamp in each reactor, and a total volume of 15 gallons. Circular wipers mounted on the lamp housing are used periodically to remove any accumulated solids formed as a result of oxidation of metals, water hardness, or solids precipitation.
In situ biodegradation with resting populations of TCE-degrading bacteria was reported as technically successful, but did not meet regulatory guidelines in the Florida pilot-test due to unexpectedly high co-contamination by chlorofluorocarbon and methane, which were preferentially degraded over TCE, and by a low oxygen content in the groundwater. This technology is most economical for large plumes with fast-flowing groundwater and low TCE concentrations (<10 ppm). Minimum ambient criteria include pore size of >10µm (to permit bacterial transport); groundwater pH of 7±1; low concentrations of TCE (concentrations of 25 ppm become toxic and populations must be frequently replenished); and dissolved O₂ must be high enough, with ranges given of 0.37-1.28 ppm depending upon contaminant and concentration). The total cost for the biofiltration process was reported to be about half of the probable pump-and-treat costs, while involving only about 10% of the volume of pump-and-treat.

Indigenous TCE-eating bacteria were collected from groundwater, cultured in surface vessels, separated from the culture media, mixed with groundwater, and re-injected into the contaminated zone. An estimated 10% of the injected bacteria attach to the subsurface soils. No nutrients are subsequently added, the organisms dependent entirely upon the pollutant for their carbon intake. The enhanced population of bacteria form a biofiltration zone below the water table through which contaminated groundwater is alternately withdrawn and injected underground ("huff-and-puff"), greatly increasing the residence time of the contaminants in contact with the bacteria.

Four major engineering considerations affect the performance of the in situ biofilter: (1) the contaminants must stay within the biofilter long enough to be degraded, hence the "huff-and-puff" pumping; (2) the degradation capacity of a given bacterial population is fixed, since no additional nutrients are provided and key biochemicals are lost during the degradation process; (3) there is a maximum number of bacteria that can be made to attach to the soil, related to the groundwater chemistry, that in turn influences residence time and degradation capacity (mainly controlled by in situ conditions); and (4) as key biochemicals are destroyed as the microbes run out of stored energy, the biodegradation reaction eventually terminates as bacteria decompose. Bench-scale testing revealed that the degradation capacity of the bacteria at the site was about 0.25 g/TCE per gram of bacteria. The thickness of the biofilter varies according to the subsurface flow and the contaminant concentration, with values ranging from under 1 cm to over 50 cm, at 20°C and 10⁵ cells/gram of sand. A 10 cm filter provided complete breakdown for 8 weeks, and had reduced degradation capacity for up to 16 weeks.

A series of laboratory experiments concluded with empirical mathematical models that predict various biodegradation parameters based on in situ conditions. Saturation, attachment rates, entrainment rates, and enzymatic longevity functions were modeled, providing quantitative data for qualitative limits on engineering parameters. Where limits exist, they are dependent upon the population longevity, the population’s degradation capacity, or the residence time of the contaminated groundwater in contact with the biofilter. Laboratory tests have shown that most soils displayed some preferential distribution of contamination to certain physical soil fractions, but the degree was not always sufficient for the fractions with lowest concentration of contaminants to be acceptable as inert
fill. Reassessing the soil in terms of contaminant mobility using the TCLP test rather than absolute concentration suggests the role of physical treatment as a preparatory stage in an overall treatment train that also involves biological or chemical decontamination.
The “Hand-D” contaminant destruction process cleans the water in two stages. In the first stage, volatile and semivolatile organic contaminants are adsorbed, and in the second stage adsorbents are regenerated in situ using an advanced oxidation process (AOP). The adsorbent was reported to have a very high capacity for TCE (up to 10 times carbon for TCE and 30 times for other VOCs), and very durable. Destruction came from complete oxidation, and advantages included on-site regeneration of the reagent and low operational costs.

Several AOP regeneration schemes were investigated, including photocatalytic destruction, $\text{H}_2\text{O}_2/O_3$, and UV/$\text{H}_2\text{O}_2$. Trials using Rohm and Haas Ambersorb 563 adsorbent and various AOPs revealed that the concept is impractical because (1) the rate of regeneration is limited by the desorption of contaminants from the adsorbent (improvements in oxidation catalysts do not improve the process) and (2) regeneration of the adsorbent required significantly more oxidant than was required for the direct oxidation of contaminants in homogeneous solution. Heating the adsorbent to promote desorption was only partially successful, requiring steam temperatures for effective desorption. The use of steam increases costs considerably, negating the potential advantages. The regeneration required constant stirring, and regeneration was ultimately limited by desorption. This meant that the regeneration process required much more Ambersorb than originally estimated, making the economics questionable.

Steam desorption of Ambersorb is already a process available from vendors using a Rohm and Haas system. In the course of the study, a significantly improved photo-oxidation catalyst was developed by doping anatase ($\text{TiO}_2$) with 1 percent platinum. This catalyst effectively destroyed chlorinated and non-chlorinated hydrocarbons in aqueous solution.
A four-year pilot-scale project was undertaken to determine whether bioventing is feasible under arctic conditions, and whether bioventing can be influenced by heating the soil. Preliminary conclusions from studying five controlled plots near Fairbanks, Alaska, are that bioventing is practical, but relatively slow, and that passive warming through black-plastic mulching of solar heat was about 1/3 the rate of active artificial warming.

Several thousand gallons of jet fuel were accidentally spilled and contaminated soil and groundwater. The groundwater table was 6 m. The conditions at the site were extreme, with average annual temperatures at 0°C (-30° to +30°C). There is no permafrost. Five plots were developed, with three warmed by hot water injection, surface electric heat tape, and passive solar warmth mulched with plastic insulation. The other two plots were controls, with no heat supplied. No nutrients or microbes were added to the plots, depending entirely upon ambient conditions.

Costs and performance will be documented in the next year's report.
Solvents and BTEX were released into an aquifer and nearby river from a former coal gasification plant. Free coal tar exists (100% pore-volume saturation) in natural stratigraphic depressions in the saturated zone. Due to problems associated with excavation, the site favored an in situ remediation process. A slurry wall was constructed to intercept further flow to the river.

The method was developed to recover petroleum from oil shale deposits, and is called “contained removal of oily wastes” (CROW). Treatability studies at this site verified 60-70% removal of coal tar, but virtually 100% of the more mobile fractions. A pattern of six injection and two extraction wells were placed in the free-product area. Hot water injection will be maintained for four months. Hot water injection reduced the coal-tar viscosity and density to less than the surrounding hot water. Oily waste and water were pumped out and cleaned on site, and the clean water was reinjected. Dense non-aqueous phase liquids are removed by gravity separation. Mobilization and recovery of the waste are determined largely by the temperature of the injected water. Lateral containment is achieved by controlling the injection and extraction rates to isolate hydraulically the affected area from the surrounding groundwater. The overall extraction rate is 570 liters per minute. The recovered residue is incinerated off-site.

The Brodhead Creek site has been selected as a Superfund Innovative Technology Evaluation (SITE) project, with close EPA-sponsored monitoring of cost and performance. These data ultimately will be published as a SITE report.
Sampling revealed very high levels of volatile organic carbons (toluene, methyl ethyl ketone, methyl isobutyl ketone in concentrations exceeding 30%), trichloroethylene and tetrachloroethylene in concentrations of 8,000 ppm, mercury (400 ppm), and lead (5,000 ppm). The Basket Creek Site, an abandoned industrial waste dump, is located in a residential area near Atlanta, Georgia. In all, about 765 m³ of contaminated soil are present with total organic concentrations of 5-10%.

A temporary building was erected over the site and all excavation and soil treatment took place within this building, which was maintained under negative pressure. Contaminated soil was excavated, screened, and treated with an \textit{ex situ} vapor extraction technology. The entire operation is designed to control volatile emissions, and only small areas (<10 m²) were opened at any time. A portable hood was placed over the excavation to facilitate vapor recovery. Vapors will be collected in a flexible duct under negative air pressure. Excavation took about twelve weeks. Soil was sized with a vibrating screen, also under vacuum. Air monitoring and sampling demonstrated that no VOCs were present outside the containment building at detectable concentrations.

Excavated soil was piled inside a temporary building to a height of about 0.6 m. Slotted well screens were placed at various elevations in the piles, and ambient air was forced through the piles to expedite vapor extraction and drying. Vapor extraction continued until VOC levels fell below 1,000 ppm total halogenated organic compounds and the soil passes the Toxic Characteristics Leaching Procedure (TCLP) for MEK and TCE. Treated soil was ultimately disposed of off site.

Extracted vapors from excavation, screening, processing, and treatment were passed through a baghouse for particulate recovery prior to thermal oxidation. Approximately 72,000 lbs. of VOCs were thermally destroyed over the course of the project. The unit is expected to demonstrate a destruction efficiency of 99%, based on sample detection limits, and cost about US$2 million.
<table>
<thead>
<tr>
<th>Title</th>
<th>Technology Type</th>
<th>Media</th>
<th>Contaminant</th>
<th>Status</th>
<th>Country</th>
</tr>
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<tbody>
<tr>
<td>Bioremediation of Petrochemicals Following a Major Fire</td>
<td>O</td>
<td>Soil/Sludge</td>
<td>Chlorinated VOCs</td>
<td>New (1994)</td>
<td>Australia</td>
</tr>
<tr>
<td>Remediation of Methyl Ethen Ketone Contaminated Soil and Groundwater</td>
<td>O</td>
<td>Surface Water</td>
<td>TPH/BTEX</td>
<td>New (1994)</td>
<td>Australia</td>
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<tr>
<td>Rehabilitation of a Site Contaminated by Tar Substances Using a New On-Site Technique</td>
<td>O</td>
<td>Air</td>
<td>Chlorinated SVOCs</td>
<td>New (1994)</td>
<td>France</td>
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<tr>
<td>Innovative In Situ Groundwater Treatment System</td>
<td>O</td>
<td>Soil/Sludge</td>
<td>Non-Chlorinated SVOCs</td>
<td>New (1994)</td>
<td>Germany</td>
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<td>Treatment of Polluted Soil in a Mobile Solvent Extraction Unit</td>
<td>O</td>
<td>Groundwater</td>
<td>Chlorinated VOCs</td>
<td>New (1994)</td>
<td>Denmark</td>
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<tr>
<td>Mobile Low Temperature Thermal Treatment System</td>
<td>O</td>
<td>Surface Water</td>
<td>Non-Chlorinated SVOCs</td>
<td>New (1994)</td>
<td>Germany</td>
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<tr>
<td>Shurry Decontamination Process</td>
<td>O</td>
<td>Soil/Sludge</td>
<td>Non-Chlorinated SVOCs</td>
<td>New (1994)</td>
<td>USA</td>
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<tr>
<td>Use of White-Rot Fungi for Decontamination of Creosote Contaminated Soil</td>
<td>O</td>
<td>Surface Water</td>
<td>Chlorinated VOCs</td>
<td>New (1994)</td>
<td>USA</td>
</tr>
<tr>
<td>Soil Washing and DCR Dehalogenation of PCB-Contaminated Sites</td>
<td>O</td>
<td>Air</td>
<td>Non-Chlorinated SVOCs</td>
<td>New (1994)</td>
<td>USA</td>
</tr>
<tr>
<td>In Situ Soil Vapor Extraction Within Containment Cells Combined with Ex Situ Bioremediation</td>
<td>O</td>
<td>Soil/Sludge</td>
<td>Chlorinated SVOCs</td>
<td>New (1994)</td>
<td>UK</td>
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<tr>
<td>Enhancement Techniques for Ex Situ Soil Separation Processes (Fine Particles)</td>
<td>O</td>
<td>Surface Water</td>
<td>Non-Chlorinated SVOCs</td>
<td>New (1994)</td>
<td>UK</td>
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<tr>
<td>Multi-Vendor Treatability Demonstration of Bioremediation Technology</td>
<td>O</td>
<td>Air</td>
<td>Non-Chlorinated SVOCs</td>
<td>New (1994)</td>
<td>USA</td>
</tr>
<tr>
<td>Integrated Pneumatic Fracturing/Bioremediation for the In Situ Treatment of Soil</td>
<td>O</td>
<td>Air</td>
<td>Non-Chlorinated SVOCs</td>
<td>New (1994)</td>
<td>USA</td>
</tr>
</tbody>
</table>
NEWLY ACCEPTED PROJECTS

The following 15 projects were accepted at the Oxford conference in September 1994 for inclusion in the Pilot Study. Three additional nominations by the United States were not accepted because they would have exceeded the limit of four projects at any one time for the United States.

<table>
<thead>
<tr>
<th>Project Title</th>
<th>Bioremediation of Petrochemicals Following a Major Fire</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location</td>
<td>Petrochemical facility, Melbourne, Australia</td>
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<tr>
<td>Project Status</td>
<td>New</td>
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<tr>
<td>Contaminants</td>
<td>BTEX, VOCs</td>
</tr>
<tr>
<td>Technology Type</td>
<td>Bioremediation (in situ and ex situ)</td>
</tr>
<tr>
<td>Technical Contact</td>
<td>S.H. Rhodes</td>
</tr>
<tr>
<td>Minenco Bioremediation Services</td>
<td></td>
</tr>
<tr>
<td>Sydney, NSW Australia</td>
<td></td>
</tr>
<tr>
<td>tel:</td>
<td></td>
</tr>
<tr>
<td>fax:</td>
<td></td>
</tr>
<tr>
<td>Project Dates</td>
<td>November 1991 - 1995</td>
</tr>
<tr>
<td>Media</td>
<td>Soil, groundwater, surface water</td>
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<td>Costs Estimated?</td>
<td>No</td>
</tr>
<tr>
<td>Project Size</td>
<td>Full scale</td>
</tr>
<tr>
<td>Results Available?</td>
<td>N/A</td>
</tr>
</tbody>
</table>

A fire in August 1991 at a petrochemical storage facility resulted in extensive contamination of soil and groundwater. Also, 12 million liters of contaminated fire-fighting water was collected and stored for subsequent decontamination. Contaminants included BTEX, phenol, methyl ethyl ketone, and others. Soil contamination with phenol was measured up to 24,000 ppm, along with high concentrations of VOCs. Laboratory testing with cultured microbes on 1 million liters of water reduced phenol concentrations from 1,400 to 50 mg/l in four days. Phenol is highly toxic to microbes in concentrations above about 4,000 ppm. Testing demonstrated, however, that the phenol toxicity could be managed using slurry bioreactors and in situ simulations. Very rapid degradation was demonstrated in the laboratory, where phenols were reduced from 11,000 to 170 ppm after 11 days. The microbial culture was prepared on site in batches and added (together with appropriate nutrients) to the contaminated water. After about two weeks, biotreatment of impounded water was complete; total phenols were reduced to <0.1 mg/l and the Microtox EC50 test showed no residual toxicity.

A field trial of the proposed process was carried out using 100 tons of soil from selected hot spots. The trial demonstrated the rate and extent of phenol removal, as well as its fate and any limiting parameters. Initial soil phenol concentrations averaged 1,200 ppm, which was reduced to <0.1 mg/L in two days. Soil microbiology revealed a 10-fold increase in total heterotrophs and phenol degraders within two weeks, then continuing increases over the trial period from 10^2 to 10^7 per gram. The pilot trial lasted 45 weeks, and resulted in a steadily declining phenol mass. After the trial period, approximately 90% of the phenol was degraded in situ and about 10% was removed by flushing (and was degraded in the recirculating leachate tank bioreactor).

In situ treatment of 1,600 m² of phenol-contaminated soil began in May 1993, with addition of controlled-release nutrients, mixing of surface soil, and regular irrigation with batches of treated water (from the bioreactor). Treatment of an additional 3,000 m² commenced in September 1993. Soil phenol levels decreased rapidly in the top 60 cm from levels as high as 1,800 ppm to below 100 ppm.
Temporary containment of organic non-aqueous-phase liquids and dissolved organic contaminants can be accomplished by manipulating bacteria in situ to produce polysaccharides (slimes), thereby reducing hydraulic conductivity around sources and providing an isolated zone for subsequent remediation. Biological clogging of aquifers is often regarded as a nuisance adjacent to boreholes, but this phenomenon can have potential benefits. Since stimulation of microbial activity can also lead to degradation of NAPLs, this bioclogging zone becomes a biologically active barrier to containment spread.

The project will determine conditions favorable to the production of polysaccharides, identify appropriate bacterial strains, and develop appropriate injection methods. The proposed study integrates research on the intrinsic bioremediation of dissolved organics and aquifer clogging by bacteria to reduce seepage.

The project will include a pilot-scale field experiment to determine the efficiency of available carbon and nutrient delivery systems to achieve optimum conditions for bacterial polysaccharide production. This will aim to reduce hydraulic conductivity enough to temporarily isolate the contaminated zone.
Significant contamination has accumulated over the years at a petroleum distribution center, resulting in plumes of methyl ethyl ketone in the groundwater. The site is being remediated using a combination of soil vapor extraction and on-site treatment of recovered groundwater and vapors. Preliminary pump testing has revealed up to 130 m³/hour flow of groundwater contaminated with up to 5,000 mg/l ketone, air stripping treatment streams up to 100 m³/hour contaminated with up to 1,500 mg/Nm³ MEK vapor, and up to 5 m³/day of recovered hydrocarbon product. Environmental regulations permit up to 300 mg/l in treated groundwater and 10 mg/Nm³ in the stack exhaust. An MEK stripper, vacuum extraction system, and afterburner were designed and built in mid-1994.

Contaminated groundwater passes through an oil/water separator prior to being air-stripped. The custom-designed stripper provides at least 90% MEK removal. Stripped groundwater is tested for compliance with standards prior to being discharged into a sewer. Contaminated air from the stripper is combined with fumes from the vacuum extraction manifold and fed to an oxidizer/afterburner, where it is burned at 760°C.

The system was commissioned in August 1994 and preliminary performance data for the customized air stripper has been reported. Even for low MEK concentrations in the influents (<1000 mg/L) a 90% removal efficiency has been obtained at temperatures ≥60°C with stripped groundwater concentrations reportedly well below the 300 mg/L limit. Unusual residual benzene concentrations of about 10 ppm in the groundwater, normally easily stripped, are probably due to the solubility of benzene in MEK.
A former coal gasification plant in Copenhagen is heavily contaminated with light and heavy tar substances, including PAHs. The project is dealing with two former tar reservoirs, which approximately measure 1,000 square meters, each with a total estimated contamination content of 12,000 tons. Analysis measurements estimate nearly 75,000 mg tar/kg soil near the bottom of the reservoirs, but most of the soil contains between 200 - 1,000 mg tar/kg soil. This project proposes to demonstrate an innovative, two-step thermal treatment of the soil, with contained air emissions. This will be the first full-scale application of this technique.

During the first step, VOCs will be removed and the overall soil moisture content reduced. The second stage will incinerate the soil at a higher temperature, degrading the SVOCs such as PAHs. The two-step process optimizes the energy use, since relatively low-cost energy is used to evaporate the ambient water. The entire treatment area (tar reservoirs as well as the treatment plant) will be enclosed in a ventilated tent. Noxious emissions will be removed using activated carbon. It is anticipated that the technique can remediate soil contaminated with up to 75,000 ppm tar, permitting reuse of the soil.

The total cost of the project is estimated to be DKK 18.1 million (ECU 2.4 million). The project is financed by EU, the City of Copenhagen, and the Danish EPA. The preliminary result from the on-site thermal treatment plant indicates that it is possible to clean tar contamination (the 16 EPA-PAH) from approximately 20,000 ppm to less than 10 ppm (99.5% cleaning).
At a former paint plant in Aubagne, tetrachloroethylene (PCE) exists in groundwater at concentrations of 3 to 4 ppm (10,000 ppm in soil). An innovative *in situ* air-stripping system will be used to remediate the groundwater to concentrations below 1 ppm. Fifteen special vapor extraction wells will be drilled in the area. These special wells consist of two co-annular wells (a small-diameter well within a larger-diameter well). The inner well extends from the ground surface into the saturated zone, and is screened in the contamination zone (approximately 27 m). The outer well extends through the vadose zone and terminates above the water table (approximately 5 m). An air injection line with a diffuser in the inner well produces bubbles of a controllable size. The rising bubbles strip the VOCs from the groundwater. Air injection is planned at a rate of 60 m³/hour, which is capable of lifting 30 m³/hour of water. The rising bubbles cause a vertical circulation of contaminated water.

A numerical model of bubble flow and phase transfer has been developed that permits estimates of flow patterns, pressure gradients, gas and water velocities, and mass transfer characteristics. According to the model, flow pattern and mass transfer of VOCs between the water and gas phases are largely controlled by bubble diameter.

This technique is estimated to be 10-15% cheaper than conventional pump-and-treat technologies, and additionally requires little maintenance, no secondary water disposal, and consolidates the contaminant into a single phase (air). Disadvantages include potential cross-contamination of a shallower aquifer and impact on groundwater levels.
A new mobile industrial pilot-scale capability is being demonstrated to treat fine soils contaminated with high molecular weight organics such as PAHs and PCBs. The soil preparation and feed system, solvent regeneration, and soil dryer are proven technologies. The innovative components include the modified flotation cells for fine particles and the separation of fine particles by controlling surface tension.

The process is expected to reduce contaminant concentration by 95-99%, and can be applied to PAHs, PCBs, pesticides, and heavy petroleum oils. The mobile pilot process, which is transported in three trailers, can be set up within two days and can handle 2-5 tons/day. The process operates under reduced air pressure, thus preventing emissions to the atmosphere. There also is no aqueous effluent. The cleaned soil contains about 10 ppm solvent, but this is easily biodegradable. During process operation the temperature of the soil does not exceed 100°C even within the soil dryer. Solvent vapors are distilled and recycled; contaminants are ultimately incinerated off-site.
A mobile, low-temperature treatment process has been developed to deal with highly volatile contaminants in fine-grained soils. This process produces virtually no waste gas and is intended to treat contaminants such as chlorinated solvents and mercury where the off-gas produced by high-temperature combustion would otherwise require further treatment and regulatory licensing. The evaporated contaminants are collected for off-site handling or disposal.

Soil screened to a particle size <15 mm is heated within a gas-tight evaporator to 290°C under continuous agitation for 30-45 minutes. Final temperature depends upon the contaminants. Steam injection is used to accelerate contaminant removal, particularly for hydrocarbons. This step essentially is a thermal phase-transfer operation, stripping the volatiles from the soil into gaseous phase. The cleaned soil is cooled and wetted (7-10% moisture), after which it can be returned to the site for reuse.

Exhaust gases from the evaporator contain a high water content, and are cooled by condensation to 5°C. Hydrocarbons and mercury are separated from the water, which is fed into a water treatment plant for use in the soil cooling unit. The contaminants themselves are separated into a light phase (low-boiling hydrocarbons) and heavy phase (high-boiling hydrocarbons and mercury), and ultimately recycled or treated elsewhere. Residual gas from the condensation step is removed with activated carbon.

Experiments have demonstrated reduction of VOCs in soil from 1,000 ppm to 0.01 ppm. Mineral oils in sand were reduced from 2,680 ppm to 10 ppm and from 38100 ppm to 61 ppm in clay. Mercury was reduced from 280 to 4.4 ppm in sand and from 11,000 to 83 ppm in clay. According to experimental data, costs of cleaning mineral oils or solvents would be about US$125/ton. For chlorinated hydrocarbons or mercury the cost might rise to $150/ton and up to US$190/ton for munitions wastes.

The mobile plant, which eliminates transportation costs and the costs associated with obtaining permits, is cost-effective for 800 tons or more of soil when compared to a fixed central facility.
A rotating fluidized-bed system has been designed to improve mixing of solids during combustion. Contaminated soil initially is screened to ≤20 mm. Oversized material is transferred elsewhere for safe disposal. Controlled elliptical circulation produces superior lateral mixing and turbulence, which also enhances combustion efficiency. Uniform temperature distributions induce complete combustion of PAHs and PCBs. The furnace operates continuously at 900°C, using fuel oil supplied at the rate of 725 liters/hour, since the contaminated soil has a negligible calorific value. A downstream flue-gas cyclone removes soil particles swept into the exhaust gas; this cyclone has a capacity of 7.5 tons/hour, and will remove up to 85% of the entrained fines. Flue gas is then passed to an afterburner (1,200°C) and quench chamber prior to being recycled to the combustion air preheater.

Gas cleaning is accomplished by adsorption in two steps. Primary adsorption of organics is accomplished by continuous addition of sorbent to the furnace, mixed in with feedstock soil. Flue gases are cooled and condensed prior to secondary inorganic adsorption. Fresh limestone is injected into the gas downstream to increase adsorption of HCl and SO₂. Entrained fines and reaction products are separated in a bag filter with further limestone adsorption.

Residual organics, including dioxins and furans as well as heavy metals, are adsorbed in two activated carbon filters. The used filters are fed back to the fluidized bed reactor.
Contaminated wet clays and peat soils are expensive to treat thermally, but are promising candidates for a slurry decontamination process. Bench-scale experimentation has documented the strengths and potential applications of the slurry decontamination process (including biological oxidation of contaminants, mobile/fixed installations, and lack of secondary wastes). The current drawbacks to the system include inadequate final decontamination levels, restriction to organic pollutants, and high price (compared to land farming).

The pilot study objectives are to design and construct a pilot plant by 1993; establish process parameters, determine costs, and design a full-scale plant in 1994; and enter the market in 1995.

Contaminated soil is mixed and sieved; coarse fractions are washed and dewatered conventionally. The fines are treated in cascading bioreactors before they are dewatered. Off-gases are passed through biological filters, and process water is recycled internally. The end product is a pressed clay cake. The pilot-scale plant has demonstrated a remediation of 3,000 to 200 ppm of oil in 60 days; the remediation proceeded very rapidly (down to 500 ppm after 25 days).
Lignin, a component of woody plants, is resistant to attack by most microorganisms. White-rot fungi have unique, nonspecific mechanisms that enable them to degrade lignin. The fungi produces several extracellular enzymes (phenoloxdases) that oxydize lignin and other complex and hard biodegradable compounds, including a wide range of pollutants.

The first part of the project was a screening test that included optimalization of growth (type of substrate, pre-treatment of substrate, water content) and evaluation of various organic additives. Underway are bench-scale radiolabelling experiments to study the production of metabolites during degradation and other bench-scale experiments to examine the stimulating effect of compost on the humification of high-weight PAHs.

Bench-scale composting experiments, planned for January to May, 1995, will compare two-phase composting (pre-optimizing soil and inoculation with fungi) to one-phase composting (inoculation without soil optimization). A pilot test, scheduled for June-November 1995 at an abandoned mine in Norway, will be conducted under optimal conditions.
One of Norway's largest energy distribution companies has a transformer-storage area contaminated with PCBs (about 1,000 metric tons). The only commercial treatment alternative, export and incineration, is prohibitively expensive. An innovative process of soil washing (for volume reduction) and DCR dehalogenation of enriched sludge is being considered for on-site remediation. The principal advantage of this process is that small volumes of wet soils can be economically treated.

After a pilot soil washing 4 m$^3$ of material, a “clean” fraction-about 70% by volume of the original material-had a PCB concentration of <10 ppm compared with untreated soil values of about 100 ppm. Bench tests have shown that soil contaminated with 1,000 ppm could be reduced to about 50 ppm using simple additives and increasing temperature and pH. In a recently completed pilot test, 4 m$^3$ of soils containing about 400 ppm PCB were treated to <10 ppm under optimal conditions, with a volume reduction of about 70%.

The DCR dehalogenation process involves two steps. In the first step, wet sludge is chemically dispersed and dehydrated with hydrophobized lime. In the second phase, a nucleophilic reagent is added that dehalogenates the matrix.

The soil will be treated at the site using a 2 tons/hour mobile washing plant. The treatment goal for the clean fraction produced by the soil washing plant has yet to be set by the regulatory authorities, but is assumed to be about 10 ppm PCB. The cleaned soil will be stored on site with a soil cap. The dehalogenation of PCB involves an exothermic chemical disintegration, after which it is dispersed into a fine powder.
<table>
<thead>
<tr>
<th>Project Title</th>
<th>In Situ Soil Vapor Extraction Within Containment Cells Combined with Ex Situ Bioremediation and Groundwater Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location</td>
<td>Abandoned Coal Processing Plant and Cokeworks, Derwenthaugh, United Kingdom</td>
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<tr>
<td>Project Status</td>
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<td>Contaminants</td>
<td>VOCs (benzene), SVOCs (phenols, PAHs), free oil</td>
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<td>Technology Type</td>
<td>Soil Vapor Extraction (in situ) and Bioremediation (ex situ)</td>
</tr>
<tr>
<td>Technical Contact</td>
<td>Paul Theile, Miller Environmental Ltd., West Yorkshire, United Kingdom</td>
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<td>Project Dates</td>
<td>1991 - 1996 (total)</td>
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<td>1993 - 1994 (this aspect)</td>
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<td>Media</td>
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<td>Costs Estimated?</td>
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<td>Project Size</td>
<td>Full scale</td>
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<tr>
<td></td>
<td>(55 ha)</td>
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<tr>
<td>Report Available?</td>
<td>N/A</td>
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This represents the first multi-process (integrated) remediation project in the U.K. The site, bounded by rivers, is designated as a strategic wildlife corridor and Site of Special Scientific Interest. Investigations have shown that the site encompasses areas of high toxicity hazardous waste, impractical to move off site. This current phase of the project, estimated to cost £2.9 million, involves the remediation of 7.9 ha encompassing the coke works portion of the site.

Both soil and groundwater are significantly contaminated with a range of oil, volatile organics (including benzene in very high concentrations), phenols, and PAHs. Evidence was found of groundwater migration off site to the adjacent River Derwent. The first stage of the remediation was to install a cutoff wall through the shallow aquifer to prevent river water from entering the site as well as to prevent the contaminant plume from reaching the river.

Free phase and vapor recovery is accomplished with vacuum extraction, with parameters established following a field trial. The field trial involved six 100 mm and four 50 mm wells drilled to 5 m depth and connected to a vacuum unit through a liquid/gas separator and activated carbon units. After 14 days of static operation, the wells then were used to gradually depress the water table. The effective radius of influence of the 100 mm wells was greater than the smaller wells, averaging 18.5 m. Following the phase I field trials, an additional 33 100 mm wells were installed for the full-scale operation, and operated for between 6 and 34 weeks. Following the dual vacuum extraction of vapor and free product, excavation commenced. A significant amount of contaminated water (100 m³/day) was extracted during the drawdown of the water table. This water was processed on site using a combination of flotation (for oil), precipitation of metals, and chemical oxidation of cyanides and sulfides, and then discharged into the river after pH adjustment and filtration. To-date, 12000 m³ of contaminated water has been treated with over 3000 kg of oil recovered.

A total of 94,000 m³ of soil will be excavated, of which 28,000 m³ is suitable for biological treatment (ex situ land farming). Following vapor recovery and dewatering of treatment cells (plots), excavation was begun and is currently proceeding. Initial analysis shows between 3.7-5.1 x 10⁶ colony forming units (CFU) per gram of soil. With naphthalene as the sole carbon source, microbial counts remain a relatively high 2-8.8 x 10⁸ CFU/g. Inorganic nutrients were added to the soil, with resulting increases in biological activity. Laboratory evaluations of parameters and optimization levels are on-going. Ultimately, cleaned soil will be encapsulated and stored on site.
Ex situ soil separation processes (often referred to as “soil washing”), mostly based on mineral processing techniques, are widely used in Northern Europe and America for the treatment of contaminated soil. The separation processes are used for removing contaminated concentrates from soils, to leave relatively uncontaminated fractions that can then be regarded as treated soil. It is beginning to be used in the United Kingdom. At present, commercial soil separation is mostly restricted to the removal of fine fractions, which normally contain the highest concentration of contaminants, leaving the coarse fractions relatively clean. However, this process is not effective where the contaminants are not concentrated in the fines, nor is it economical where the fine fraction constitutes a significant proportion of the soil mass. Enhancement of soil separation processes and the development of downstream processes for treating fine fractions are necessary to increase the range of soil types treatable by soil washing and to reduce the volume of secondary wastes that require disposal.

This project will use samples of actual contaminated soils representative of sites in the United Kingdom. Contaminants will include both organics and metals. Considerable effort has been spent on developing laboratory characterization and pilot-scale monitoring procedures for the separation treatment of contaminated soils. This work will be extended to investigate and critically review process-enhancement alternatives to identify economical ways to reduce treatment volumes. The project will investigate how fines inhibit soil washing by considering initial materials handling and feed preparation, including evaluating opportunities for improving feed preparation and downstream liquid/solid separation of these fines.

Laboratory and pilot-scale work will be completed by August 1995 and a final report, considering the technical feasibility of full-scale applications, likely treatment costs, and potential market factors, will be completed by November 1995.
This orphan site, located in the town of Sweden, near the city of Rochester, New York, was used for the disposal of drummed liquid wastes. More than 2,400 drums have already been removed from this site. The residual contamination will be treated using conventional excavation and low temperature thermal desorption unless one of the alternative treatment technologies being demonstrated proves to be cost-effective. Three competing technologies were selected from 13 proposals. Two of these technologies treat only soil while the other treats soil and groundwater. The requirements for the demonstration only specified soil treatment.

The first technology is an *in situ* bioventing process consisting of 27 wells connected to an air extraction unit. There are an equal number of injection and extraction wells. The injection wells deliver necessary ammonia and methane nutrients. The second technology involves two identical *ex situ* “biovaults” in which contaminated soils are placed. Nutrients, moisture, pH, temperature, and oxygen levels are controlled. The first biovault is being operated under aerobic conditions and the second is switched between aerobic and anaerobic conditions. The second biovault will allow both oxidizing and reducing conditions to develop and will be used to assess the impact of reducing conditions on biological degradation of chlorinated contaminants. The third technology is a vacuum-vaporized well process that uses *in situ* bioremediation to treat saturated and unsaturated zones and groundwater contaminated with VOCs. Naturally occurring microorganisms will be used. An *ex situ* bioreactor will be used for off-gases. The system, contained within a 0.4 m diameter well, comprises a submersible circulation pump, bioreactor, and an air source to strip volatiles and enhance biodegradation. The system is designed to treat an extended volume of soil by groundwater circulation. This system is capable of adapting to the site's fluctuating groundwater levels.

This project was proposed to NATO/CCMS because of its unique approach in using competition and demonstration as part of the remediation process. The biovaults and bioventing testing were completed in December 1994. Analytical data from the last sampling event has been received and is being analyzed. Final reports are expected by July 1, 1995. The vacuum-vaporized well processes will continue through October 1995.
The objective of this project is to demonstrate that fracturing of low permeability strata will increase permeability and lead to enhanced *in situ* biodegradation. The microbial population will be stimulated by injected nutrients and oxygen. BTEX concentrations in the soil range from 120-150 ppm. The target is 95% reduction within the top 1.6 m of soil.

The pneumatic fracturing process involves the injection of high-pressure air at controlled flow rates in the contaminated zone. This process will create conductive channels in the formation. The vapor movement in the formation becomes controlled by convection and diffusion instead of by diffusion alone, thus increasing permeability and the exposed surface area of the soil.

*In situ* biodegradation conditions for maximum rates and durations will be determined for indigenous microbial populations, and seed cultures will be developed if necessary. A pneumatic fracturing system with the capability of injecting microbes already has been designed. The system also will employ pneumatic fracturing to enhance stacked aerobic, denitrifying, and methanogenic microbial processes in staggered spatial distribution for maximum effectiveness. Aerobic processes will dominate at the fracture interfaces. Depletion of oxygen during aerobic biodegradation will allow the formation of methanogenic populations at greater distances from the fractures. Produced methane will be diffused out with the pneumatic sweep air.
“Solidification Application: Solidification of Fly Ash Samples Coming from Solid Waste Incineration Plant” (1993) Ayse Filibeli, Dokuz Eylul University, Izmir, Turkey

The application of solidification/stabilization technologies to the treatment of fly ash from a domestic solid waste incineration plant was reported. Fly ash samples taken from the electrofilters of a plant near Trimmis, Sweden were tested with a number of solidification mixes and reagents. At present fly ash from the plant is “washed” before being sent to the disposal area representing an increased cost of about 6 to 8 DM per metric ton of domestic solid waste. Solidification was evaluated as a more cost-effective alternative to “washing.”

Fly ash samples taken from the incineration plant were solidified by the addition of additives including cement, calcium oxide, calcium hydroxide, gypsum, and sodium silicate. After a curing period of 28 days the solidified samples were tested for compressive strength and for the leaching of contaminants using the German DIN tests.

The majority of solidified samples had compressive strengths of at least 500 kN/m². Leaching test results showed that a high proportion of the pollutants were fixed within the solidified mass. The costs of the solidification process was in the order of 0.21 to 2.7 DM per metric ton of domestic solid waste suggesting that this process may represent a cost-effective alternative to fly ash “washing.”


A detailed review of chromium geochemistry, toxicology, chemical analysis, was conducted to identify potential remedial strategies for sites contaminated with chromium wastes. An in situ treatment for reducing chromium (VI) to chromium (III) was suggested.

“Prediction and Optimization of the Abiotic Environment in Landfarms to Enhance Biodegradation” (1994) Jan Freijer, University of Amsterdam, Amsterdam, the Netherlands.

Mathematical models combined with simple, inexpensive laboratory methods were used to predict biodegradation processes and landfarm scenarios such as effect of treatment compared to non-treatment; determining the rate-limiting thresholds for hydrocarbon concentration; and predicting the biodegradation rates for given soil parameters.

Landfarming was described as an ex situ bioremediation process for soils contaminated with petroleum hydrocarbons. Contaminated soil is typically excavated and spread on an impermeable foil in layers of about 1 m. Biodegradation is stimulated by aeration, irrigation and drainage, mixing, and adding nutrients and heat. The solid phase is immobile while the aqueous and gaseous phases are mobile. Landfarming is a common European technique because of its environmental and economic advantages.

Present research is focused on optimizing the biodegradation process as well as developing improved monitoring methods and evaluating the risk associated with the residual materials. Chemically, the degradation of hydrocarbon contaminants occurs through the biological oxidation of the hydrocarbon into biomass and the release of CO₂ and water. This reaction is commonly referred to as “mineralization” of hydrocarbon. Criteria for mineralization include the presence of non-chlorinated hydrocarbons, inorganic nutrients (N, P, K) are not rate-limiting, O₂ and water are present, and an appropriate temperature.

The use of mathematical models was reported to simulate the dynamics of environmental parameters in soils, in quantifying the microbial response to the environmental factors thus computing a degradation rate, and applying calibrated models to evaluate various treatment scenarios in landfarms. Three deterministic, one-dimensional transport models (gas, heat, water) and one empirical biodegradation
model were developed. Simple laboratory measurements of transport coefficients were used to calibrate the models, and boundary conditions were assumed from typical landfarming scenarios. Models were evaluated at existing experimental landfarms in large outside lysimeters. The distribution of substances and energy in soils is governed by transport processes that determine the biodegradation rate.

Research will concentrate on refining and simplifying field methods to monitor biodegradation rates to reduce costs, as well as to introduce new data sets into current models to refine them and quantify uncertainties.

“Controlled In Situ Groundwater Treatment” (1994) James F. Barker, University of Waterloo, Waterloo, Ontario, Canada.

Plumes of groundwater contamination extend from sources commonly present in the subsurface (DNAPLs or LNAPLs), even below the water table. Many of these subsurface sources of contamination are very difficult to remediate. Pump-and-treat can provide an effect means of hydraulically containing the sources; however, at many sites pump-and-treat will have to continue for many decades because the source zones dissipate slowly. Projected long-term operation and maintenance costs are therefore large.

A new approach for source-zone and plume containment that is more passive and that offers considerable potential for long-term cost savings is contaminant treatment using permeable, in situ treatment zones. Aspects of this approach have been developed by the University of Waterloo (Canada). A treatment zone, or “wall,” is composed of permeable material placed across the contaminant plume. The desired treatment is generated by either flushing the required chemicals into the wall or by having the required chemicals emplaced as solids in the wall. Another approach is the “funnel-and-gate” system (patent pending). In this system, low permeability vertical barriers are placed across plumes. Gaps, or “gates,” in the barrier allow passage of the plume through a reactive medium so that the water is treated while passing through. The objective is to cause the plume to meet water quality standards on the down-gradient side of the system.

University researchers have developed various approaches for in situ treatment of a wide variety of common organic and inorganic groundwater contaminants, including chlorinated solvents, petroleum-derived contaminants such as BTEX, metals, nitrate, and phosphate. Intensive laboratory and several prototype field trials have been conducted. Designs for full-scale systems have been developed and several means of installing the systems compatible with various geological and geotechnical conditions are now available for unconsolidated or semi-consolidated deposits to depths of over 30 m. Design options for funnels range from sealable joint steel piling to conventional soil-bentonite slurry walls. Options for gates include permanent installations of reactive media to easily removable cassettes of reactive materials that are positioned in the gates for a specified period and conveniently replaced later when reactive material is consumed. In some systems, plumes with complex contamination are treated in gates having a series of reactive media.

“U.S. Air Force Bioventing Initiative” (1994) Andrea Leeson, Battelle-Columbus, Columbus, Ohio, U.S.A.

Bioventing is the use of subsurface injection and withdrawal of gases to stimulate biodegradation. The technique frequently results in volatilization; soil venting (also known as soil vacuum extraction) frequently results in biodegradation. Bioventing is useful to treat nonvolatile biodegradable contaminants and to improve the performance and economics of biodegradation.

The Air Force is demonstrating the effectiveness of bioventing at 138 sites across the country, collecting cost and performance data. As of September 1994, 121 sites have been tested, 92 systems are running, and 50 sites have been operational for at least one year. The goal is to obtain nationwide regulatory acceptance of the technique. Data will ultimately be used to produce, jointly with the U.S. EPA, a bioventing design manual.
Field treatment consists of a six-stage protocol: (1) a soil-gas survey for baseline characterization; (2) Install vent well, monitoring points, and a background well; (3) conduct in situ soil-gas permeability tests; (4) conduct in situ respiration tests; (5) install a 1 to 2½ horsepower blower; and (6) conduct long-term bioventing tests (for one year). The soil gas survey is applicable to shallow sites (3-4 m), since it is useful only if the probes penetrate to treatment depths. Soil sampling, part of the site characterization, tests for total petroleum hydrocarbon, BTEX, total phosphorous and Kjeldahl nitrogen, iron, moisture, particle size, pH, and alkalinity. Optimal pH is in the 5-9 range; alkalinity may affect apparent respiration rates due to CO₂ production. In situ respiration testing measures O₂ utilization rates over time together with He loss, which is an indicator of leakage around monitoring points. Respiration testing compares respiration rates within the contaminated zone to those outside the zone, and measures the oxygen diffusion out of the area. Results from an in situ respiration test at Johnston Island in the Pacific revealed a biodegradation rate of 19 mg/kg/day. The radius of influence of bioventing was defined as that area to which adequate air can be supplied to meet O₂ demand. It is determined by measuring O₂ after equilibrating pressure changes.

BTEX compounds were the most significant contaminant, but most sites had <1 mg/kg. No clear pattern emerged from initial and one-year measures of soil BTEX concentrations. Aeration was found possible at most sites (90%), and biological respiration was observed at all sites. Inorganic nutrients (such as nitrogen) were usually present in ambient concentrations enough that feeding was unnecessary. Site limitations that affected bioventing success include high moisture content in the soil, inadequate permeability, and temperature. The most significant problem was permeability, which was also related to soil moisture content. Cleanup levels were not determined.

“Danish Assistance in the Remediation of Tököl Airbase” (1994) Jens Nonboe Andersen, Rambøll, Hannemann & Højlund, Virum, Denmark

Large quantities of free-phase jet fuel have been recovered from Tököl, considerably reducing the health risk posed by the contamination to nearby well fields. However, free-phase product cannot be recovered completely, and adsorbed contaminants in the unsaturated zone contribute to on-going threats to public health. Successful pilot-scale demonstration of an in situ bioventing system at the site resulted in the decision to proceed with full-scale in situ remediation.

Tököl Airbase, located 20 km south of Budapest, was occupied by the Soviet military from the late 1940s to mid-1991. Hungarian environmental authorities became aware of extensive soil and groundwater contamination at the facility (see page 14). Contamination was primarily jet fuel in four discrete zones. Free-phase contamination in one zone alone covered a volume of over 2,000 m³.

Since the fall of 1991, the Danish EPA has been assisting the Hungarian Ministry for Environment and Regional Policy in conducting site investigations and remedial response to the contamination. The most significant phase of the assistance, following emergency intervention and logistical support, has five components: (1) risk assessment of the consequences of the contamination to the potential impact on human health and to determine appropriate remedial actions; (2) control and recover the free-phase jet fuel and minimize further contamination or dispersion; (3) monitoring trends over time of the free-phase as well as soil and groundwater contaminants; (4) modeling groundwater flow and contaminant transport and dispersion in three dimensions in order to predict contaminant migration to the Danube River (12-18 years) and to the nearby well fields (6-12 years); and (5) demonstrate a pilot-scale system for biological in situ remediation of the contamination at the airbase, and design scale-up parameters for full-scale remediation.
NATO/CCMS FELLOWS

Germany


After German reunification, the Federal Government gave the new Länder of Germany (the new states of Mecklenburg-Western Pommerania, Berlin, Brandenburg, Saxony-Anhalt, Saxony, and Thuringia) the opportunity to establish an exemption clause that removes the liabilities of owners or investors of commercial properties from environmental damages caused prior to July 1, 1990, at the discretion of the responsible state government. The purpose of the exemption clause is to accelerate economic development in the new Länder by removing some of the problems to potential investors of contaminated land. Exemption may be granted after the interests of the purchaser, the general public and the environment have been considered. Approximately 69,000 applications for exemption have been made. Financing the remediation of contaminated sites in the new Länder was agreed to in December 1992 by the Federal Government and the new German states. In cases where the site owner has been exempted from the liability of environmental damage the costs of remediation will be shared by the Federal Government (60% share) and the new Länder (40% share). A budget of DM1 billion per year for ten years has been committed to these projects. The objective of this fellowship is to review and monitor experiences with large remediation projects in the new Länder. Examples of such projects include the remediation of 50 ha site at Rositz, Thuringia which is contaminated by phenols, PAH's, BTEX-aromatics, and aliphatic hydrocarbons. The site had been used between 1917 and 1990 for the processing and conversion of 17.5 million metric tons of lignite tar and 9 million metric tons of crude oil into petroleum products. There are 19 such large remediation projects documented throughout all six of the new German states.

Portugal

- Maria Teresa Chambino, INETI, Lisbon, and Maria Jose Macedo, Institute of Materials Science, Oeiras. *Review of the Contaminated Land Situation in Portugal.*

An on-going study by the Institute of Environmental Technologies (INETI) is examining soil contamination arising from the use of coke ovens and its potential for remediation. The first phase of the work has involved quantifying the total area of contamination and the range of concentrations of contaminants present within the soils at these sites. In particular, a detailed characterization of the organic contaminants present in the soils is being conducted along with an evaluation of the bioremediation of this contaminated material. Site investigation has revealed high concentrations of polycyclic aromatic hydrocarbons (PAHs) and cyanides within the site soils.

Turkey

- Resat Apak, Istanbul University, Istanbul. *Sorption/Solidification of Selected Heavy Metals and Radionuclides from Water.* See pages 18, 46

United Kingdom


The Phase II Pilot Study will produce a final report after its conclusion in 1997. This fellowship will coordinate the organization, technical consistency, and quality assurance of the various chapters that constitute the final report. At the Oxford meeting in September 1994, committees were formed to develop working
instructions for authors and principal investigators to follow in the preparation of draft and final reports.


- Mary Harris, Clayton Environmental Consultants, Ltd, Berkhamsted.  *Costs of Remediation and Implications for Technology Transfer.*

The systematic collection of economic information on remediation technologies is critical for the wider application and acceptance of technically proficient technologies. Further, such data would allow a comparative assessment of alternative technologies of similar technical capability and improve the effective transfer of technologies across international borders. The objectives of this project are to identify the most sensitive cost elements according to the economic conditions of the host country and to develop a framework that differentiates these elements. This framework will be assessed using demonstration project data to produce a report on the implications of cost for technology transfer.


The objective of this project is to discover the fundamental reasons why many emerging technologies fail at hazardous waste sites. It will focus on the air sparging technology. Air sparging tends to channel through soil pores with the largest radius, whether the system is pulsed or not. Hence the distribution of air in the sparged zone is not uniform and difficult to predict.
NATIONAL CONTACTS

Pilot Study

Directors

Walter W. Kovalick, Jr., Ph.D.
Technology Innovation Office
U.S. Environmental Protection Agency
401 M Street, SW (5102W)
Washington, DC 20460
United States
tel: 703-308-8800
fax: 703-308-8528

Stephen C. James
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
26 West Martin L. King Drive
Cincinnati, Ohio 45268
United States
tel: 513-569-7877
fax: 513-569-7680

Co-Directors

Volker Franzius
Umweltbundesamt
Bismarckplatz 1
D-14193 Berlin
Germany
tel: 49/30-8903-2496
fax: 49/30-8903-2285

Esther Soczó
RIVM/LAE
P.O. Box 1
Antonie van Leeuwenhoaklaan 9
3720 BA Bilthoven
The Netherlands
tel: 31/30-743-065
fax: 31/30-293-651

Country Representatives

Ian Lambert
Environmental Protection Agency
40 Blackall Street
Barton Act 2600 Canberra
Australia
tel: 61/6-274-1696
fax: 61/6-274-1230

Harald Kasamas
Federal Ministry of Environment, Youth and Family
Untere Donaustrasse 11
A-1020 Vienna
Austria
tel: 43/1-21132-5315
fax: 43/1-21132-5020

Jacqueline Miller
Institut de Sociologie
GEHAT
Université Libre de Bruxelles
44 Avenue Jeanne
1050 Bruxelles
Belgium
tel: 32/2-650-3183
fax: 32/2-650-3189
George Hill
Environment Canada
Unit 100
Asticou Centre
241 Cité des Jeunes Blvd.
Hull, Québec K1A 0H3
Canada
tel: 819-953-8718
fax: 819-953-4705

Inge-Marie Skovgaard
Danish Environmental Protection Agency
Waste Deposit - Groundwater Division
29 Strandgade
DK-1401 Copenhagen K
Denmark
tel: 45/3-266-0100
fax: 45/3-296-1656

René Goubier
Polluted Sites Team
ADEME
B.P. 406
49004 Angers Cedex 01
France
tel: 33/41-204-120
fax: 33/41-872-350

Volker Franzius
Umweltbundesamt
Bismarckplatz 1
D-14193 Berlin
Germany
tel: 49/30-8903-2496
fax: 49/30-8903-2285

Róbert Reiniger
National Authority for the Environment
Alkotmány ut. 29
H-1054 Budapest
Hungary
tel: 36/1-201-1725
fax: 36/1-201-4282

Esther Soczó
RIVM/LAE
P.O. Box 1
Antonie van Leeuwenhoaklaan 9
3720 BA Bilthoven
The Netherlands
tel: 31/30-743-065
fax: 31/30-293-651

Raymond Salter
Resource Management Directorate
Secretary for the Environment
Ministry for the Environment

84 Boullcott Street
P.O. Box 10362
Wellington
New Zealand
tel: 66/4-473-4090
fax: 66/4-471-0195

Semund Haukland
Norwegian Pollution Control Authority
P.O. Box 8100 Dep
Sørumsveien 96
N-0032 Oslo
Norway
tel: 47/22-57-34-00
fax: 47/22-67-67-06

Branko Druzina
Institute of Public Health
Trubarjeva 2-Post Box 260
6100 Ljubljana
Slovenia
tel: 386/61-123-245
fax: 386/61-323-955
Ingrid Hasselsten  
Environmental Protection Agency  
17185 Solna  
Sweden  
tel: 46/8-799-1444  
fax: 46/8-799-1222

Urs Ziegler  
Federal Office of the Environment, Forests, and Landscape  
Federal Department of the Interior  
Buwal Laupenstrausse 20  
3003 Berne  
Switzerland  
tel: 41/31-322-9338  
fax: 41/31-382-1546

M. Reşat Apak  
Professor of Analytical Chemistry  
Istanbul University  
Avcilar Campus  
Faculty of Engineering  
Istanbul 34840  
Turkey  
tel: 90/1-5911-996  
fax: 90/1-5911-997

Judith Denner  
Contaminated Land and Liability Division  
Department of the Environment  
A228 Romney House  
43 Marsham Street  
London SW1P 3PY  
United Kingdom  
tel: 44/71-276-8348  
fax: 44/71-276-8403

Walter W. Kovalick, Jr.  
Technology Innovation Office  
U.S. Environmental Protection Agency  
401 M Street, SW (5102W)  
Washington, DC 20460  
United States  
tel: 703-308-8800  
fax: 703-308-8528