Announcement

The First INTERNATIONAL CONGRESS on PETROLEUM CONTAMINATED SOILS, SEDIMENTS & WATER
14-17th August, 2001 • Imperial College, London, U.K.

Topics of Interest

• Analytical methodologies - laboratory & field
• Clean-up technologies for marine & coastal oil spills
• Compensatory determination for crude oil & hydrocarbon contamination
• Cross-country comparison of contamination standard, & standard setting approaches
• Ecological impact & risk assessment
• Environmental fate & modeling
• Environmental forensics
• Environmental issues for production water from production activities
• Fuel additives and oxygenates
• GIS application
• Human risk and health analysis
• Innovative technologies
• International comparison of contamination regulations and policies

• International laws and cooperation issues on contamination monitoring and clean-up
• International clean-up technology transfer & issues
• Natural Resource Damage Assessment (NRDA) of marine & terrestrial contamination
• Pollution minimization & prevention techniques for production, processing, transportation & storage
• Remediation technologies: bioremediation, chemical extraction, composting, phytoremediation, stabilization, etc.
• Risk-based clean-ups (RBCA)
• Site assessment /field sampling
• Soil chemistry
• Sources & levels of crude oil and hydrocarbon contamination
• Case studies of above related subjects

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Cover photos courtesy Enzyme Technologies, Inc., Portland, Ore.
"The Remediators” research group in CSIRO Land and Water in Perth, Western Australia have investigated contaminant behavior in groundwater and soil environments, and remediation strategies for contaminated sites for over a decade. The focus of the group has been in situ remediation techniques for organic contaminants, but they have also evaluated natural attenuation processes, ex situ (above ground) remediation strategies, and innovative in situ/online monitoring instrumentation.

The group has carried out laboratory-scale proof-of-concept and field-scale demonstration and evaluation of:

- air sparging for volatile contaminants in groundwater
- bioventing for in situ bioremediation
- permeable reactive barrier technologies for a range of contaminants
- bioventing to temporarily contain mobile contaminants
- multiphase extraction of petroleum products (non-aqueous phase liquids or NAPL)
- phytoremediation (use of plants)
- natural attenuation of a range of contaminants in groundwater and soil environments

**Air Sparging**

A series of air sparging (air injection below the groundwater table) trials has been carried out for dissolved gasoline constituents in groundwater and for residual non-aqueous phase liquid (NAPL) gasoline, ie separate phase. Initial trials indicated that dissolved benzene and other gasoline contaminants could be removed from groundwater within hours to days, but that the zone of effectiveness was within a 2 to 4-m radius of the air injection (sparging) well. Most cleanup was found to be due to volatilization or physical stripping, rather than due to enhanced bioremediation from stimulation of aerobic bacteria by oxygen in the injected air. For the NAPL sparging trial, soil vapor extraction alone was found to remove only a small percentage of the total mass removed, compared to air sparging combined with soil vapor extraction. Another outcome of the work was that no significant reduction in the aquifer hydraulic conductivity was observed, even though residual air was found to be still at significant levels in groundwater some nine months after air sparging had ceased.

**Bioventing**

Bioventing was evaluated as a cleanup technique for diesel fuel contamination. Air and nutrients (ammonia and phosphate) were periodically injected into a diesel-contaminated zone 3.7 to 4.5 m below ground, to stimulate aerobic biodegradation. Over a 14-month period, biodegradation rates increased by a factor of 5-10 from background rates, i.e. up to 90 mg-diesel/kg-soil/day. Phospholipid analysis of soil materials showed that microbial biomass increased dramatically where nutrients and air (oxygen) were present. Ammonia was transformed to nitrite and nitrate, and was utilized variably in the contaminated zone. Most locations showed reductions of diesel concentrations in soil cores, with preferential biodegradation of some of the diesel constituents. At some locations, diesel concentrations were reduced to below 1,000 mg/kg from starting concentrations 100-fold higher.

**Permeable Reactive Barriers**

Permeable reactive barriers (PRBs) offer the potential to treat groundwater in situ, with the potential for lower long-term maintenance costs. The principle is reasonably simple and involves placing a subsurface permeable barrier across the direction of contaminated groundwater flow. The intention is to treat the contaminants of concern within the barrier and allow cleaned groundwater to flow downstream beyond the PRB. The reactive portion of the PRB may be a range of treatments from aeration or addition of reductants (such as carbon) to stimulate biodegradation, to zero-valent iron that abiotically degrades chlorinated solvent chemicals.

CSIRO has shown proof-of-concept for PRBs for atrazine (a herbicide), petroleum hydrocarbons, and ammonium.
plumes in groundwater. Field-scale evaluations of PRBs have commenced, although few are complete. A dual barrier approach has been devised for the ammonium PRB concept. In this dual approach, oxygen is delivered in the first PRB to convert ammonium to nitrite/nitrate and a reductant (such as hydrogen or ethanol) is delivered in the second PRB to convert the nitrite/nitrate to harmless nitrogen gas. This is successfully occurring in laboratory-scale soil columns, and a field site has been instrumented with a small PRB to test the concept. It is hoped such a technique will knock out ammonium in groundwater that would otherwise discharge to the marine environment along the west coast of Western Australia. It is planned to expand this work for other contaminants, such as metals.

**Multiphase Extraction of Petroleum Product (Non-aqueous Phase Liquids or NAPL)**

Petroleum hydrocarbon liquids (non-aqueous phase li-

uids or NAPL) are notoriously difficult to recover from subsurface soil and groundwater environments. Failing to remove all of a NAPL gasoline, for example, may provide an ongoing source of soluble benzene (and other compounds) to groundwater flowing past the NAPL, for possibly decades. CSIRO has carried out field trials for enhancing NAPL recovery. These trials involved separately and simultaneously pumping the groundwater to induce drainage of NAPL to the recovery borehole, skimming/pumping of the NAPL product itself, and applying a vacuum to the well to recover vapors and avoid excess lowering of the water table.

In the initial field trial in the sandy aquifers in Perth, applying a vacuum during groundwater pumping increased the recovery by greater than 5-fold compared to recovery while only pumping groundwater. Further field trials are planned, and especially to assess recovery efficiencies during low and high water tables, since NAPL
thickeneses in recovery boreholes can vary significantly seasonally.

**Phytoremediation to Hydraulically Isolate and Remediate Soil and Groundwater**

Plants are being increasingly trailed to remediate metals and hydrocarbon contaminated soils and groundwater. The Perth CSIRO group are one year into a field trial using eucalyptus trees (River Red Gums, Tasmania Blue Gums, etc) to hydraulically isolate and remediate petroleum contaminated soil and groundwater. The study has a dual aim: (i) to determine if the trees can reduce leaching of contaminants to groundwater and perhaps reverse hydraulic gradients in groundwater, and (ii) to determine the enhanced biodegradation potential in treed plots compared to an unplanted control area. It is early days, so no conclusive data are yet available. Other CSIRO groups have successfully carried out field trials on the uptake of selected metals into plants.

**Natural Attenuation (NA)**

Natural attenuation stands with other technologies as a valid remediation/management option, where attenuation processes (biodegradation, dispersion, etc) can reduce contaminant concentrations below criteria at compliance boundaries (ie property boundaries, rivers, oceans, human exposure, etc). For a range of contaminants, nature may be able to do a better job at cleanup, than can be achieved by human intervention - ie. nature may be able to cope. For some contaminants, chemical loadings are too high, or biogeochemical conditions are not conducive to high-enough attenuation to be effective as a management strategy.

The CSIRO group has quantified at field scale the natural attenuation of gasoline compounds, solvents, munition residues and some pesticides. Some of these contaminants do degrade naturally given the right geochemical and microbiological conditions, but some do not. They have found, for example, at a gasoline-spill site in Perth that benzene under sulphate-reducing conditions shows only limited signs of attenuation, but toluene is readily attenuated (biodegraded). They have modelled the biogeochemical processes to determine the eventual fate of the gasoline plume. A current project seeks to determine the attenuation potential for petroleum hydrocarbons as they move towards a river environment, and especially at the groundwater/river water interface.

**Innovative Measurement and Monitoring**

Often detailed site characterization and monitoring is required to properly implement and evaluate remediation (whether enhanced or natural). The CSIRO group has developed in-field techniques and on-line monitoring to assist in this task. They have trialed partitioning tracer techniques for quantifying the gasoline NAPL distribution and saturation in the zone of water table fluctuation - this technique promises to provide repeatable measurement of NAPL distributions in the subsurface.

They have developed on-line probes for measuring volatile organic compounds and oxygen - these probes can be buried at multiple locations and depths in soil or groundwater environments, and data can be reported remotely to the web. They are currently in use to monitor the effectiveness of air sparging remediation, to determine the fate of gasoline vapors in soil profiles and beneath houses, and to quantify the effectiveness of a geosynthetic capping strategy.

**More Information**

For more information about The Remediators see the groups web page at: www.clw.csiro.au/research/remediation/organic/ or e-mail: Greg.Davis@per.clw.csiro.au. The group also organized the 1999 and 2000 Contaminated Site Remediation Conferences held in Fremantle and Melbourne.

Principal supporters of the groups research are BP, Western Australian Industry Groups, Shell, BHP, Rio Tinto, the Water and Rivers Commission of Western Australia, and the Centre for Groundwater Studies.

*Dr. Greg Davis is with CSIRO Land and Water, Center for Groundwater Studies, Wembley, Western Australia.*
Phytoremediation is the direct use of living green plants for in situ, or in place, risk reduction for contaminated soil, sludges, sediments and groundwater, through contaminant removal, degradation or containment. Growing and, in some cases, harvesting plants on a contaminated site as a remediation method is an aesthetically pleasing, solar-energy driven, passive technique that can be used to clean up sites with shallow, low to moderate levels of contamination. This technique can be used along with, and in some cases in place of, mechanical cleanup methods.

How Does Phytoremediation Work?

Phytoremediation (phyto means plant) is a general term for several ways in which plants are used to clean up, or remediate, sites by removing pollutants from soil and water. Plants can break down or degrade organic pollutants or contain and stabilize metal contaminants by acting as filters or traps. Some of the methods that are being tested are described in this article.

Phytoextraction, also called phytoaccumulation, refers to the uptake and translocation of metal contaminants in the soil by plant roots in the above ground portions of the plants. Certain plants, called hyperaccumulators, absorb usually large amounts of metals in comparison to other plants.

Rhizofiltration (rhizo means root) is the adsorption of precipitation onto plant roots or absorption into the roots of
contaminants that are in solution surrounding the root zone. Rhizofiltration is similar to phytoextraction, but the plants are used primarily to address contaminated groundwater rather than soil.

*Phytostabilization* is the use of certain plant species to immobilize contaminants in the soil and groundwater through absorption and accumulation by root, absorption onto roots, or precipitation within the root zone of plants (rhizosphere). This process reduces the mobility of the contaminant and prevents migration to the groundwater and air, and reduces bioavailability for entry into the foot chain.

*Phytovolatilization* is the uptake and transpiration of a contaminant by a plant, with release of the contaminant or a modified form of the contaminant to the atmosphere from the plant.

Phytoremediation is a new and exciting approach to cleaning up groundwater pollution and soil contaminants using different species of plants as the primary component. This method is low-cost, environmentally friendly and effective for a wide range of chemicals such as pesticides, solvents, crude oil, polyaromatic hydrocarbons and metals as well.

**Case Studies**

**Equilon Enterprises/Shell Development**

This pilot project, located in Houston, uses hybrid poplar to remove chemical pollutants from the soil. Currently they have a Flow32 sap flow system with TDP sap velocity probes attached to measure the water used by a stand of hybrid poplar trees planted over a contaminant plume. They employ a SunScan LAI (Leaf Area Index) system in order to extrapolate the plant water use to the entire plot. AM100 portable leaf area meter is measuring the total leaf area of some trees to do indexing. Results so far look very good.

**BASF and Walsh Environmental**

This project is located in Baton Rouge, La., where they are using Black Willow trees to remove...
a photodegradable herbicide contaminant from the soil. The objective is to model the process in order to replicate the project to other sites and be able to predict results and time requirements to complete remediation. They have a Flow32 sap flow system with a Dynamet weather station attached to calculate ETP. A DL2e datalogger with TDP probes, DEX dendrometers and ThetaProbes track key parameters of sap velocity, growth rate, and soil moisture conditions.

In this case, it works out well that the chemical is photodegradable and breaks down when it reaches the leaves of the willows. There is no need to remove, store or incinerate the contaminant.

Roy F. Weston/Lockheed/EPA

Roy F. Weston, Inc., and now Lockheed of Edison, N.J. is performing a study for the EPA at Aberdeen Proving Ground in Maryland. They have had good success with the Dynagage and TDP probes in measuring sap flow of poplar trees. Early indications show that the trees use water at a faster pace than the groundwater can move off the site. Remarkable results showed that the trees were able to contain the contaminant plume. Potential recommendation from EPA include that sap flow be a standard part of a phytoremediation project monitoring in order to meet EPA guidelines.

This project was updated at the Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May, 2000, Monterey, Calif. The data and groundwater modeling indicated:

- 156 poplars, over 2034 m² - 1/3 ac.
- Sap flow, tree size, canopy and on-site weather examined seasonally over three years.
- Sap flow measured in the first two years with Dynagage (Dynamax heat balance sensors) collars.
- Sap flow measured for two latest years with TDP (Dynamax thermal dissipation sap flow probes) needles.
- ETP evapotranspiration computed on a daily basis for three years from weather data.
- Leaf area and projected Leaf Area Index (LAI) estimated from growth progression.
- Sap flow, LAI and ETP combined to produce a site specific "crop index".
- Separate groundwater level monitoring and groundwater modeling confirm an area of depression within the poplar plantation.

"Ongoing monitoring of groundwater levels revealed a conical depression within the plantation area implying tree induced hydraulic containment. A 3-D groundwater flow and transport model was then implemented to assess the capacity of the remedial program to hydraulically contain and ultimately reduce the VOC plumes. The model

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required the calculation of tree water removal rates over a 30 year period and site sap flow data were analyzed for this purpose. the collection of tree transpiration data at a phytoremediation site, combined with an understanding of site hydrology, provides important information regarding the efficiency of phytoremediation in providing plume control.” (Dale M. Haroski, Lockheed Martin; Steven R. Hirsh, EPA, Philadelphia; John G. Wrobel U.S. Army Garrison, Aberdeen, Md.; Harry R. Compton, EPA/ETRC, Edison, N.J.)

Phytoremediation Checklist

Here is a summary of recommendations for equipment to proceed with phytoremediation projects proposed by Dynamax. this equipment proposal is produced in order to satisfy the main components of interest in most phytoremediation projects: 1) groundwater surface fluctuations and water balances, 2) plant growth and stress factors, and 3) soil microbial activity measurement.

Transpiration - Environmental Fluctuations

Plant cover can account for up to 95% of the water leaving the soil and is the most important factor in measuring evapotranspiration. In order to accurately know how much water the plants are using, you can use a Flow32 sap flow system. The system tells you in “real time” (grams or kilograms per hour) the transpiration rate of the plants. With this information, you will know whether or not the plants are using water fast enough to prevent the contaminant plume from migrating off the site and the phytoextraction rates.

In this approach, the plant water use is indexed to the leaf area or to the stem or trunk cross-sectional area. This allows you to extrapolate per plant water use to a land area basis, or to the total number of plants present over the site.

The plant sap flow can be indexed to the ETP calculations from the DynaMet weather station to make projections of annual plant water use. Sap flow data is taken periodically in blocks of 7-14 days throughout the season and is indexed to the ET calculations from the weather station. Based on continuous weather data, one may develop the crop index method of accurately forecasting water consumption, and therefore the extraction rates. With this approach, it is not necessary for the researcher to be at the site all the time, but could take measurements once every two or four weeks.

In addition to the sap flow system, an expansion kit or a separate datalogger with ML2 Theta soil moisture probes (buried at different depths) may be used to do a soil moisture profile and track the soil water level movement.

Another phytoremediation method includes pumping contaminated water to irrigate plants and to encourage the establishment of new plants. Clearly the soil moisture measurement is a key item for scheduling this application of water to prevent runoff and to maintain appropriate moisture for the plant itself.

Plant Growth and Stress

DEX Electronic Dendrometers can monitor the plant growth rates or stress levels over periods of 1-2 months continuously. This sensor can measure stem or fruit diameter changes as small as 0.050 mm. the data represents diurnal changes and gives a very accurate measure of the growth rate over a longer projection. Declining diameter indicates a stress level of the plant. The researcher knows “when” plant stress occurs and “how much” stress is present.

Oxygen and Carbon Dioxide in Soil

Measuring the amount of oxygen and carbon dioxide in the soil is a direct indicator of the biotic activity present. the 2250 high resolution gas analyzer and SRC soil respiration chambers will measure the soil respiration rate. the equipment can be left in place to make continuous measurements or periodically moved around to other sites to get sample data over the whole test area. This data will give a very good idea of how much microbial activity is present in the soil and how this may change over time.

Mike van Bavel is President of Dynamax, Houston, Texas.
Remediation Retrofit: Achieving Groundwater Treatment Goals Using Dissolved Oxygen In Situ Treatment (DO-IT)

By David Laughlin and Brian Clark, P.E.

In situ biological treatment, or bioremediation, has been increasingly successful as a remedial application, especially as new products and systems are being developed to better support the biological degradation process. One such process, known as enzyme-catalyzed Dissolved Oxygen In Situ Treatment (DO-IT), is consistently proving itself extremely effective at in situ treatment of petroleum hydrocarbon contaminants, including methyl tertiary butyl ether (MTBE). This article discusses the problems associated with MTBE remediation, and summarizes the retrofit of a pump and treat (P&T) system with the revolutionary DO-IT technology. Using this supplemental remediation approach, site soil and groundwater cleanup goals for dissolved BTEX and MTBE were achieved within one year.

MTBE... Why so difficult?

As concern about MTBE contamination in groundwater continues to grow, the need for remediation technologies capable of treating this compound becomes more critical. In comparison to petroleum products, MTBE poses significant problems when it escapes into the environment through gasoline releases, typically from underground storage tank (UST) systems, aboveground storage facilities, or pipelines. MTBE is capable of traveling rapidly through soil, is much more soluble in water than most other petroleum constituents, and is considered more resistant to biodegradation. Therefore, it often travels farther than other gasoline constituents, making it a more likely threat to impact public and private drinking water wells.

Because of its solubility in water and, consequently, its tendency to form large contaminant plumes, petroleum releases with MTBE are more difficult, costly, and time-intensive to remediate than petroleum releases that do not contain MTBE. Furthermore, traditional remediation methods such as pump-and-treat, soil vapor extraction, and air sparging have had difficulty showing consistent MTBE reductions. However, the DO-IT process has successfully achieved MTBE treatment at numerous sites, including use as a retrofit of existing treatment systems that have reached their performance limits.

How the Technology Works

Bioremediation is the process of using bacteria and other biological enhancements under controlled conditions to convert organic compounds (in this case, petroleum hydrocarbons) to carbon dioxide, water, and energy for
cell production. The enzyme-catalyzed DO-IT process promotes this process by using proprietary biological products in combination with a highly specialized in situ oxygenation equipment platform to obtain rapid reduction of petroleum contaminants. The biological enhancements includes a proprietary multi-enzyme complex solution that significantly increases the rate of contaminant degradation by catalyzing the conversion of aromatic and aliphatic hydrocarbons to fatty acid. In combination with a highly specialized TPH-specific bacterial consortium, petroleum hydrocarbons are degraded to the end-products of carbon dioxide and water.

As with most in situ bioremediation efforts, contaminant degradation is usually limited by the amount of available oxygen (the electron acceptor in aerobic biological processes). Therefore, the DO-IT technology includes a unique equipment platform, the BioBox, which contains a specialized pure-oxygen mixing process that generates high-dissolved oxygen water at concentrations of approximately 40 ppm. These dissolved oxygen levels are approximately four times what conventional systems can provide; since oxygen is usually rate limiting, the DO-IT technology can effectively quadruple the rate of contaminant degradation. The BioBox injects the oxygenated, biologically-amended water into the subsurface for continuous support of biological degradation. For treatment of adsorbed soil contamination in the vadose zone and the hydraulic zone of fluctuation ("smear zone"), the DO-IT process includes vapor-phase air/oxygen injection capability. This feature provides unlimited flexibility for site applications.

The ideal DO-IT application is a closed-loop extraction/enhancement/re-injection scenario, which recycles the oxygenated treatment water throughout the zone of contamination. This provides biological contact and support, improving in situ treatment efficiency and decreasing overall treatment time. The following paragraphs summarize a DO-IT retrofit at a Connecticut gasoline station.

Site Treatment... A Definite Challenge

The site is an active gasoline station property located in a rural area, with a surface water stream downgradient from the contaminant plume. Previous gasoline releases occurred on the site as a result of leaky dispenser piping. Subsequent site characterization activities indicated MTBE and BTEX contaminants as well as gasoline-range

Figure 1. Connecticut gas station site plan.

Figure 2: Total BTEX Reductions
Gasoline Station Site, Connecticut

<table>
<thead>
<tr>
<th>Compound</th>
<th>GA GPC for Groundwater</th>
<th>GA PMC for Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1.0 ug/L</td>
<td>20 ug/kg</td>
</tr>
<tr>
<td>Toluene</td>
<td>1,000 ug/L</td>
<td>20,000 ug/kg</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>700 ug/L</td>
<td>10,100 ug/kg</td>
</tr>
<tr>
<td>Xylenes</td>
<td>530 ug/L</td>
<td>19,500 ug/kg</td>
</tr>
<tr>
<td>MTBE</td>
<td>100 ug/L</td>
<td>2,000 ug/kg</td>
</tr>
</tbody>
</table>

Table 1.
petroleum constituents in the soil and groundwater. Remediation of contaminated soil and groundwater at the site was necessary to control any off-site migration and potential impact to the downgradient stream.

A P&T system was installed in the mid-1990s. After four years of operation, the system had achieved only marginal contaminant reductions, with no additional mass removal evident (based on site groundwater and system O&M data). The DO-IT process was retrofitted to the existing P&T system in an effort to reduce groundwater contaminant concentrations to the desired regulatory levels.

The original contaminant plume exhibited a flowpath along the natural south-southeast groundwater gradient, and covered approximately 8,000 square feet. The hydraulic zone of fluctuation, or "smear zone," was approximately 3–4 feet annually. The groundwater lies within a silty sand matrix at approximately 6–8 feet bgs. Four main groundwater monitoring wells, MW-3, MW-5, MW-8, and SP-1 exhibited BTEX and MTBE contamination. A general site plan is shown in Figure 1.

**Treatment Goals**

The Connecticut Department of Environmental Protection (CTDEP) rates the groundwater aquifer as GA (denotes a potable potential-use aquifer), which requires cleanup to GA Groundwater Protection Criteria (GA GPC). Soil contamination is regulated by the GA Pollutant Mobility Criteria (GA PMC) limits. Table 1 summarizes these regulatory limits.

Groundwater (and soil) monitoring was the independent responsibility of the environmental consultant on the project. This monitoring was performed quarterly for most monitoring points. All laboratory results were independently analyzed by an accredited, licensed laboratory.

**The Ideal Supplement**

The critical application component for any in situ bioremediation project is adequate contact of the biological enhancements with the contaminants in the soil and/or groundwater. As discussed above, the DO-IT process uses a liquid extraction/enhancement/re-injection scenario to accomplish this contact. For this site, the DO-IT process was installed as a retro-fit of the existing P&T system. The site consultant utilized as much of the existing infrastructure as possible, including extraction wells and pumps. Vertical injection points were installed throughout the plume and the capture zone of the extraction wells. This DO-IT system also included an integrated bioreactor component for groundwater treatment prior to re-injection.

This layout allowed for both hydraulic control of the dissolved-phase contaminants and continuous movement of the treated groundwater (with dissolved oxygen, bacteria, and nutrient amendments) throughout the site. Monitoring wells within the contaminated plume were used to measure remedial progress. No injection into the monitoring/sampling points was performed, so that representative data points could be maintained throughout treatment.

**System Operation**

An initial inoculation with the enzyme complexes and the specialized TPH-degrading bacterial consortium was performed in mid-1999.
Since that time, the DO-IT system has performed automatic oxygenated water injection into the vertical injection points on a near-continual basis. Additionally, enzymes and the TPH-degrading bacterial culture are continuously metered into the oxygenated water to maintain a healthy degrading biological population. Water samples are collected monthly and/or quarterly to monitor both the nutrient concentrations and the bacterial plate count population within the aquifer. When water samples indicate deficient nutrient levels, a specialized nutrient blend is added to the injection water and applied to the subsurface.

Treatment Results

Significant degradation of the benzene, MTBE and TPH compounds was reported after the first 90 days of treatment. Contaminant degradation continued throughout 1999 and early 2000, as illustrated in Figures 3 and 4. Currently, benzene and MTBE levels in all wells are below the GA GPC limits for groundwater. Furthermore, recent soil sampling results also indicate degradation of all BTEX, MTBE, and TPH constituents below the GA PMC soil limits. DO-IT system operation is ongoing, with anticipated shutdown within 2-3 months.

With the DO-IT system, MTBE is being successfully degraded. The groundwater sampling results from this site show rapid and complete degradation of dissolved-phase MTBE. This capability by the DO-IT process has been verified under laboratory studies, and is being successfully utilized at other sites. Initial results at these sites further exhibit the effectiveness of the DO-IT technology for MTBE treatment as well as TPH cleanup.

Conclusions

In situ bioremediation, through the use of the DO-IT system, has achieved remarkable treatment of dissolved-phase benzene and MTBE compounds as well as adsorbed-phase BTEX and TPH contaminants. The success of this in situ bioremediation project can be attributed to a number of factors, including 1) consistent addition of highly active bacterial and enzyme enhancements, 2) process support from the automated DO-IT platform (for continuous site-wide oxygenation and process control), and 3) a well-designed injection/extraction system by the site consultant.

The integrated application of the DO-IT technology has resulted in rapid and effective groundwater cleanup of the MTBE, BTEX, and petroleum contaminants. The DO-IT process is a proven treatment system that should be considered when analyzing remedial alternatives for any petroleum-contaminated site. As this discussion illustrated, the DO-IT technology can be an extremely effective supplemental treatment component to any existing remediation system, and may be the answer to achieving your site cleanup goals.

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Facts and Fallacies: Petroleum Degradation in a Subsurface Environment

By Dan McNicoll, Luc Paul Tousignant and Philip Augustine

The relationship (if any) between the age of petroleum found in the subsurface and its non-weathered condition was considered during a recent environmental arbitration. The arbitration involved a major petroleum company (vendor) and a commercial wholesale distributor (purchaser). At stake was the legal and financial responsibility for approximately $2,600,000 in soil and groundwater remediation. The petroleum company took the position that because the petroleum product encountered within the subsurface had a non-weathered gas chromatographic (GC) profile, the petroleum was of recent origin. On this basis, the petroleum company denied legal and financial responsibility for the clean-up of contaminated soil and groundwater at the subject site. The wholesale distributor argued that while, superficially petroleum product exhibiting a non-weathered GC profile would appear to imply that the petroleum product was of recent origin, that conclusion is not necessarily correct and is subject to numerous local conditions. The following article will present a case study of the arbitration, a description of the various factors affecting weathering of free petroleum product, a discussion on the effectiveness of age dating of hydrocarbons and the arbitrators ruling/conclusion.

Case Study

The subject site consisted of two former bulk petroleum storage facilities which were situated side by side (one immediately north of the other) on a 14 hectare piece of property, located in the City of Ottawa, Ontario (Photo 1). In the mid 1980s, a major petroleum company acquired the two petroleum facilities and subsequently decommissioned them both during the late 1980s.

Geological Conditions

The northern and southern portions of the site are underlain by a brown, fine-to-medium grained sand of post glacial origin (Richard et al., 1967). Thin, grey, silty sand and silty clay units are found interbedded within the sand throughout the site. The local groundwater table is at an average depth of five meters below grade. A perched water table was also encountered in one area of the southern portion of the site at a depth of approximately two meters below grade. The local groundwater regime was calculated to have an average hydraulic gradient of approximately 0.01 m/m in a north-easterly direction.

Northern Site

Upon decommissioning the petroleum storage facilities on the northern portion of the site, the petroleum company retained an environmental consultant to assess whether the underlying soil and groundwater regimes had been adversely impacted from the past operation of the facility. After several subsurface investigations were undertaken, the consultant concluded that the site met provincial standards. Based on their conclusions, the petroleum company sold the northern portion of the site to a third party. Subsequently, this portion of the site was found to have extensive groundwater contamination, which was characterised by both dissolved phase and free phase petroleum product. The petroleum company gave the new purchaser assurances that it would remediate the site.

In the fall of 1990, the petroleum company conducted a major remediation program involving a major excavation to remove the free petroleum product from the surface of the groundwater. At the conclusion of the excavation, the consultant for the petroleum company concluded that all free product had been removed from the subsurface of the site. In order to treat the dissolved phase groundwater contaminant plume, the consultant installed, operated and monitored a groundwater pump and treat system. In 1991, while the groundwater pump and treat system was

Photo 1. Aerial view of the former bulk petroleum terminals situated on the northerly and southerly portions of the site in the mid 1980s.
still being operated and monitored by the petroleum company's consultant, the northern site was sold by the third party to the commercial wholesale distributor (purchaser).

In 1992, free petroleum product was discovered in an existing monitoring well on the northern portion of the site (hereinafter referred to as monitoring well N1). This monitoring well was located beneath the northern former bulk petroleum storage facility and was situated immediately adjacent a former above ground diesel storage tank.

The petroleum company immediately claimed that the petroleum product in N1 was a result of vandalism for which it was not responsible. The petroleum company claimed that the petroleum product was introduced into the subsurface sometime after it completed its remediation attempts. The petroleum company claimed that the petroleum product negated all of its past remedial efforts and thus it was no longer responsible for any further on-site remediation and ceased dissolved phase remediation on the northern portion of the site.

**Southern Site**

The petroleum company had an initial investigation completed of the southern site by their same consultant. Based on the results of their investigations, the consultant concluded that the southern portion of the site met acceptable provincial criteria.

Prior to the wholesale distributor (purchaser) completing the purchase of the southern property, Trow Consulting Engineers (Trow), was retained to verify the subsurface conditions of the site on behalf of the purchaser. Trow found free petroleum product floating on the surface of the groundwater regime and heavily contaminated soil beneath portions of the site. Faced with these facts, the petroleum company acknowledged that the site did not meet acceptable provincial criteria and accepted responsibility for the remediation of the site. With this commitment in hand, the commercial purchaser completed the purchase of the southern site in 1991, but held back approximately 50% of the purchase price pending successful completion of the remediation by the petroleum company.

In the summer of 1991, the petroleum company completed a major soil excavation program on the southern portion of the site. The primary focus of the remediation program was to recover the free petroleum product from the surface of the groundwater table and remediate the soil and groundwater regimes to acceptable provincial criteria. In an attempt to reduce costly landfill disposal fees, the petroleum company's consultant attempted to treat the contaminated soil on-site using enhanced volatilization techniques.

Over the next 5 years, the petroleum company performed no less than four additional remediation attempts to bring the southern portion of the site into compliance with provincial regulations. All of these additional remedial attempts focused on near surface (<3-4 m) soil contamination. Verification studies performed by OMM/Trow and others showed each time that the remedial attempts failed to attain the desired remediation objectives.

In 1996, free petroleum product was encountered in a newly constructed monitoring well on the southern site (hereinafter referred to as monitoring well S1) which was located beneath a part of the southern former bulk petroleum storage facility. Once again, the petroleum company claimed vandalism was the source of the free product discovered in S1 and terminated all site remedial efforts.

The petroleum product in both the N1 and S1 monitoring wells was measured, at times, to be up to 0.4 m in thickness. A free product sample was collected by Trow from monitoring well S1 and submitted to an environmental laboratory for characterization. The laboratory found the petroleum product to have a chromatographic profile similar to that of non-weathered diesel fuel.

**Remediation by Purchaser**

In order to proceed with the development of the site, the commercial purchaser took it upon itself to remediate both the northern and southern portions of the site. Trow was retained to design and supervise the construction of an innovative, partially subgrade bioremediation facility which was used to treat the contaminated soil from both portions of the site in two separate batches. The bioremediation facility, or bioreactor, incorporated the use of the A.M.O.E.B.A.™ Process - a bioremediation technology developed by Trow for the federal government in 1994. The system also incorporated an elaborate on-site groundwater treatment system to treat the dissolved phase groundwater contaminant plumes underlying both the northern and southern former bulk petroleum storage facilities.

**Arbitration**

The commercial purchaser sought monetary reimbursement from the petroleum company for the cost of the final site remediation programs, which it undertook. The petroleum company refused to reimburse the commercial purchaser and the parties agreed to submit the matter to arbitration.

**Petroleum Company's Position**

The petroleum company took the position at the arbitration that the free petroleum product discovered in the northern portion of the site in 1992 and in the southern portion of the site in 1996 was unrelated to the sites previous use as bulk petroleum storage facilities. As a result, it denied liability for the site remediation costs incurred by the commercial purchaser. The petroleum company relied on the following arguments in support of their position. It claimed:

- That the non-weathered nature of the petroleum product indicated that the product was recently introduced into the subsurface. The petroleum company retained the services of a well-known forensic chemist who supported the company's contention that the product was recent in age. The forensic chemist even went as far as claiming that the product was between three and five years old (i.e. after the commercial purchaser had purchased the property).
- That prior to the discovery of petroleum product in monitoring well N1 in 1992, free product had not been previously detected in this well. Furthermore, it claimed that the dissolved groundwater concentrations within this well had been improving as a result of the ongoing groundwater pump and treat system installed in the vicinity of this well.
- That all of the free petroleum product had been successfully recovered during the 1990 and 1991 initial remedial excavations, thus the 1992 and 1996 occurrences had to be unrelated to past site use.

Since no obvious source for the free petroleum product existed on-site, the petroleum company simply attributed the presence of the product to possible acts of vandalism.

**Commercial Purchasers Position**

The commercial purchaser claimed that the petroleum company failed to achieve an acceptable level of soil and groundwater remediation on this site and thus, the petroleum company was still financially responsible for the final site remediation program, which was undertaken by them. In essence, the position of the commercial purchaser was that the discovery of free petroleum product in 1992 and 1996 was simply residual product which remained on the
surface of the groundwater regime due to the incomplete remedial efforts undertaken by the petroleum company. The product was drawn into the monitoring wells by the operation of their groundwater pump and treat systems. Arguments made in favor of their position included the following:

- Free product was historically used on-site and was found to be present on the surface of the groundwater regime, prior to initial clean-up attempts undertaken by the petroleum company in 1990 and 1991;
- Initial and subsequent remediation programs undertaken by the petroleum company between 1990 and 1996 were incomplete and unsuccessful due to: i) the lack of proper initial site characterization studies to delineate the full extent of the free petroleum product plumes, ii) the failure to collect soil verification samples of the walls and base of the remedial excavations, iii) the failure to obtain an adequate number of soil verification samples of the treated soil prior to it being used as backfill material, and iv) the failure, in at least one situation, to establish the remedial objective criteria prior to undertaking the remediation program.
- Prior to the occurrences of free product in N1 and S1, the petroleum company's own consultant documented the presence of petroleum product on the surface of the groundwater table at several locations after the major attempt at recovering the free petroleum product was undertaken in 1990 and 1991;
- No evidence of vandalism existed to support the presence of the product in N1 or S1 originating from the introduction of petroleum product onto the ground surface or into existing monitoring wells (which were always locked);
- No on-site sources of petroleum product existed hydraulically up-gradient from this location;
- Field notes taken by the petroleum company's consultant indicated that free petroleum product was sporadically present in monitoring well N1 with the first observations being made before the 1990 remedial attempt;
- Field notes taken by the petroleum company's consultant also indicated that free petroleum product was in fact present on the surface of the groundwater table in the area of the 1990 excavation after it was backfilled (i.e. after they claimed to have recovered all of the product);
- The non-weathered chromatographic profile of the petroleum product was attributed to:
  a) The relatively deep groundwater table (>5m) which would limit fresh, oxygenated surface water from reaching this zone. Without this source of oxygen, biological processes would likely have been inhibited or greatly reduced;
  b) The presence of low conductivity zones (i.e., silty sand and silty clay lenses) within the native soil which could have served as a confining layer - effectively minimizing or preventing volatilization of the more volatile fractions of the petroleum product; and,
  c) The silty sand and clay lenses may have also served to deflect any surface water infiltration and groundwater away and/or around the petroleum product plume further preserving it from weathering processes.

Factors Affecting Petroleum Product Degradation

The degradation (weathering) of hydrocarbons in the subsurface is affected by three main processes. These processes are biological, chemical and physical.

Biological Processes

Hydrocarbons will be most significantly degraded by biological processes in conditions which permit the proliferation of biological organisms. These conditions can be affected by the following:

Contaminant Concentration

When the concentration of contaminants reaches a certain level, it inhibits microbial growth. The level of microbial inhibition varies from one contaminant to another. For example, when free petroleum product is encountered in the subsurface, the concentration of the contaminant is usually so high that it is often toxic for the microorganisms. Although biodegradation of free petroleum product can occur in these circumstances, it would most likely be restricted to the interface of the petroleum product and the groundwater. At that location the hydrocarbon will usually be present in the dissolved phase and therefore be more readily available for microbial uptake (Stout and Lundegard, 1998).

Temperature

Temperature can have profound effects on the biodegradation rates of hydrocarbons in the subsurface (McNicoll and Baweja, 1995). Temperature affects the metabolic rate of microorganisms, the volatilization rates of hydrocarbons (the higher the temperature the higher the volatilization rate), the solubility of the compound and the composition of the microbial community (Leahy and
Colwell, 1990). As a rule-of-thumb, the rate of biodegradation is halved for every 10°C decrease in temperature (this is known as the Q10 rule - Metcalf and Eddy, 1979). From the above rule-of-thumb it is apparent that an increase in temperature (up to the microorganisms preferred range) increases the biodegradation rate. Likewise, a decrease in temperature decreases the rate of biodegradation.

**Nutrients**
The level of nutrients in the host soil and/or groundwater can affect biodegradation rates of hydrocarbons. Low levels of nutrients such as nitrogen and phosphorus in soil (ie sands) or groundwater can significantly reduce the rate of biodegradation (Leahy and Colwell, 1990).

**pH**
Most bacteria and fungi prefer near neutral pH conditions with fungi being more tolerant of acidic conditions. Extremes in pH will generally have a negative impact on the availability of microorganisms, which degrade hydrocarbons. Typically a pH between six and eight is preferred by microorganisms (Leahy and Colwell, 1990).

**Oxygen**
Most biodegradation of hydrocarbons and other organic contaminants occurs aerobically and this, by definition, requires oxygen. Due to the hydrophobic nature of hydrocarbons, it is likely that no water will be present in free product found in the subsurface and therefore no dissolved oxygen will be present. In aerobic degradation systems, oxygen is usually the rate limiting parameter affecting biodegradation (Leahy and Colwell, 1990).

**Physical and Chemical Processes**
Physical and chemical processes can also affect the degradation or weathering of petroleum product. These processes include:

**Solubility**
The solubility of hydrocarbons in water is a very important parameter when studying the movement and degradation of a petroleum product plume. Volatilization and biodegradation rates of hydrocarbons are strongly affected by their solubility. For instance, microorganisms must first produce enzymes to dissolve hydrocarbons in order to biodegrade them. If the product is partially dissolved, the task of assimilating them is made easier for the microorganisms. As well, the more soluble hydrocarbons will more readily travel in the groundwater thus reducing the concentration of the product plume and increasing the rate of degradation. The aqueous solubility of hydrocarbons decreases with an increase in the carbon number.

**Soil Organic Matter and Adsorption**
Organic contaminants tend to adsorb onto organic matter. Adsorption controls the quantity of free organic chemicals in solution thus governing a contaminant's mobility, persistence and bio-availability. This results in a removal of mass from the free product plume.

**Volatilization**
Volatilization can remove mass from the product before other processes even commence (Tousignant, 1990). This is especially the case when dealing with hydrocarbons (such as gasoline) which have a relatively high percentage of volatile compounds (i.e., Benzene). Volatilization rates are affected by soil properties (such as soil type and permeability), local environmental conditions (such as soil moisture content, temperature, etc); and the chemical and physical properties of the petroleum product.

**Moisture Content**
Moisture content plays an important role in adsorption mechanics since water molecules compete with organic molecules for adsorption sites on soil particles. An increase in moisture content decreases the adsorption of hydrocarbons. Water molecules compete poorly with non-polar molecules for hydrophobic surfaces in soil organic matter. In other words, despite the moisture content, hydrocarbons (which are non-polar hydrophobic molecules) will readily adsorb on the hydrophobic sites of soil organic matter thus making these hydrocarbons unavailable for microbial uptake.

In summary, due to the toxic nature of petroleum product to biological processes, the physical and chemical processes are often the predominant mechanisms, which affect free petroleum product degradation, or weathering, in a subsurface environment.

**Age Dating**
Hydrocarbons encountered in the subsurface are often analyzed using a gas chromatograph (GC). The GC provides a profile of the hydrocarbon which when equated (i.e. area under curve is calculated), the concentration of the hydrocarbon can be determined. The GC profile can also provide some indications as to whether hydrocarbon is weathered or non-weathered. Non-weathered hydrocarbons have a profile, which is characterized by a series of long spikes extending above a bell shaped curve or "hump". Weathered hydrocarbons show fewer long spikes on the hump or, in extreme cases, just the hump. The theory which underlies the age dating of hydrocarbons is that the more weathered the hydrocarbon GC profile (i.e. the fewer the long spikes), the older the petroleum product.

The fallacy of this theory is apparent if one considers the dramatically different weathering patterns which would be experienced by two samples of petroleum product if one were kept away from oxygen in a dark cool place and another which was exposed to oxygen, warm temperatures and sunshine. Clearly, after a period of time the two samples, despite being the same age, would show marked differences in weathering. Notwithstanding the obvious unreliability of co-relating weathering and age there seems to be a wide spread misconception that if petroleum with a fresh or non-weathered GC profile is found in the subsurface it must be of recent origin. This was the theory advanced by the petroleum company in the above noted case study.

According to Senn and Johnson (1987), the presence of high concentrations of light end compounds would be indicative that the product has no been in the soil for an extended period of time. However, this paper is only intended as a general guide to the interpretation of gas chromatograms. It would be fair to say that the absence of light end compounds from a gas chromatogram indicates that a certain degree of weathering has occurred. This, in effect, demonstrates that the site conditions favor weathering (biological, physical and/or chemical). However, the presence of light end hydrocarbons or fresh product by no means implies that the spill is recent (Christian and Larsen - 1993). The Senn and Johnson (1987) paper warns against the erroneous interpretation of gas chromatograms without due consideration of the site conditions.

According to Stout and Lundegard (1997) when free product above the groundwater is present, biodegradation appears to be greatest in the zones below the oil-water interface where pore saturation with diesel is lowest. They suggest that bioremediation is favored in this zone since contact
with flowing groundwater occurs (i.e. delivery of dissolved oxygen is made possible and dissolved hydrocarbons may thus be degraded). Curtis and Lammey (1998) go on to suggest that the presence of fresh free product in an old plume can be explained by an "insulating effect" occurring around the core of the plume. They explain that the fringes of the plume suffer some degree of weathering and thus have their viscosity affected which in turn creates a "shell" around the core of the plume thus preventing the mixing of the shell and core products. Therefore, the middle of the plume remains unaffected.

Christian and Larsen (1993) describe other reasons for the preservation of the plume freshness. They explain that the conditions generally found inside an oil affected body inhibit microbial growth. These conditions include low nutrient concentrations, low levels or complete absence of oxygen and high contaminant concentrations that may be toxic to soil microorganisms. The effect that these conditions can have on a product freshness is well described in Wang et al. (1998) were relatively fresh product was encountered in 25 year old contaminated soil.

To summarize, free product in a soil column above the water table can remain relatively unchanged due to a variety of factors. The most important ones being: 1) the concentration of the product may be toxic to the microorganisms, 2) the presence of free product saturated soil means that the soil pores are filled with free product and, because of the hydrophobic nature of hydrocarbons, dissolved oxygen present in the groundwater and infiltration water cannot reach these areas, 3) the weathering of the plume fringes cause a difference in product viscosity thus creating a protective "shell" around the core of the plume thus isolating it.

Arbitrator's Ruling

During the lengthy arbitration process, the petroleum company spared no expense at trying to support their "non-weathered means recent" argument including the calling of evidence from four expert witnesses. Upon examining all of the evidence, the arbitrator concluded that the most likely source of the petroleum product was the historical petroleum storage tank facilities. The presence in 1992 and 1996 of free product (some of which was non-weathered) was, he concluded, simply the result of incomplete remedial efforts by the petroleum company. The arbitrator did not concur with the argument that the non-weathered nature of the product meant that it was recent. He cited with approval the evidence of two of the experts called for the purchaser. Commenting on one such expert, the arbitrator stated: "I accept [the purchaser's expert] evidence that one can not determine the age of [petroleum] product based upon weathering. If [petroleum] product is sheltered from oxygen, for example, being buried deep in the ground, it could be very old and not be weathered. The fact that the product is not weathered does not tell whether it is old or new."

The arbitrator concluded that the petroleum company did not prove that the unwethered petroleum product was of recent origin. In fact, the arbitrator went on to state: "I cannot and do not accept (petroleum company's forensic chemist) testimony that the free product found at (51) was less than five years old. On all of the evidence in the case, it had to be older than that."

This finding (and others) by the arbitrator ultimately led to his decision that the petroleum company was legally and financially responsible for the contamination on the sites and ordered that it pay the commercial purchaser approximately $2,600,000 for the remediation of the property. In addition, the petroleum company ultimately paid a substantial portion of the commercial purchasers legal fees in this matter.

Conclusions

Based on the facts of the case study and the arbitrator’s ruling, it is evident that one cannot assume that non-weathered free petroleum product found in the subsurface means that the product is recent in age. There are some scientific references available suggesting that under certain conditions old product can remain unwethered for many, many years (Stout and Lundegard, 1998; Wang et al., 1998). These articles however all suggest that this phenomena tends to occur in the center of a relatively thick (i.e. several meters) petroleum column. In this particular case, the product thickness did not exceed 0.4 m of thickness and thus would appear to be markedly different from case studies that have been previously noted in literature.

Based on the results of this case study, it is evident that an environmental investigator cannot simply look at the chromatographic profiles of a petroleum product to assess its relative age. Rather, one must carefully consider all factors ranging from product type to host conditions and carefully weigh all of these factors before making any age-related statements pertaining to free product in the subsurface.

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Bioremediation Accelerates Brownfield Cleanup

By Mike Saul and Michelle Broyles

Bioremediation, using Cl-out microbes, clears the obstacles to Brownfield redevelopment by reducing contaminant concentrations in groundwater and removing the environmental stigma from the property. The Cl-out bacteria were selected for their ability to degrade a wide range of organic chemicals under aerobic conditions. Cl-out bioremediation of chlorinated solvents does not produce harmful breakdown products such as vinyl chloride.

Background

Cl-out is comprised of patented Pseudomonas species, which were isolated from a contaminated site in northern United States. These species have the ability to reduce chlorinated organic contaminants, such as tetrachloroethylene (PCE) and trichloroethene (TCE) under aerobic conditions. Breakdown of PCE under aerobic conditions has been previously thought impossible to achieve, but lab studies and field applications have proven differently. PCE and TCE are broken down completely under aerobic conditions, without harmful byproducts.

The theoretical pathway for chemical break down is based on the anaerobic pathways that have already been established. Cl-out oxidizes chlorinated chemicals using a cometabolic metabolism, which requires the addition of dextrose to trigger the reactions. A dehalogenating enzyme first removes one chlorine atom from PCE, which has four chlorine atoms total, to produce TCE. This allows oxygenases enzymes, probably monoxygenases (MMO), to oxidize TCE forming an epoxide, which is further oxidized to 1,2-dihydroxy-TCE. Then 1,2-dihydroxy-TCE is oxidized completely to carbon dioxide, fatty acids, and water.

Cl-out is produced in a freeze-dried form and packaged in 55-gallon bags. Once the Cl-out is hydrated it can be applied under light pressure through one-inch injection wells (vertical or horizontal), within 24 hours of adding water to the bag.

Field Applications

Enhanced Natural Attenuation

The suite of chlorinated contaminants found in ground water at an engraving facility suggested the partial anaerobic degradation of tetrachloroethylene (PCE) and trichloroethene (TCE). The solvents were historically used in the 1970s to clean equipment in the facility and may have been released to the environment during handling. Once in the soil and ground water, the solvents were partially degraded to cis-1, 2-dichloroethene (cis1, 2-DCE) and vinyl chloride. The relative concentrations are shown on figure 1. The natural degradation appeared to have stalled at cis-1,2-DCE and vinyl chloride, which is typical in anaerobic degradation. Studies have shown that vinyl chloride and possibly cis-1, 2-DCE more readily degrade under aerobic conditions, which the aquifer may have been unable to sustain.

The risk-based closure criteria, required significant reduction of the cis 1,2-DCE and vinyl chloride concentrations. Combined aeration and bioaugmentation were implemented to treat the groundwater. The combination of
these technologies was used to provide aerobic microbes shown to be capable of degrading the target chemicals and an associated oxygen-rich environment suitable for this bioremediation pathway. Cl-out microbes were added initially without aeration in January 2001. After the initial inoculation, the cis 1,2-DCE concentrations decreased from 193 to 46 ppb with little change in the vinyl chloride concentration. Aeration was added in February and the aquifer was re-inoculated with Cl-out microbes. The following monthly samples showed both the cis-1, 2-DCE and vinyl chloride concentrations decreased to less than detection limits (2 ug/L).

This project demonstrates that Cl-out bioremediation combined with air sparging may be used to polish off the products of natural anaerobic biodegradation to make a natural attenuation remedy feasible. The total cost for implementing this bioremediation project was less than $20,000.

**Dry Cleaning Facility Achieves Clean Closure**

Soil and groundwater contamination resulted from improper solvent handling at a 50-year old dry cleaning facility. After the initial site investigation, the accessible contaminated soil was excavated, but there was residual contamination in the bottom and sides of the cavity that could not be excavated due to proximity to the building. Several groundwater samples taken from monitoring wells beneath and adjacent to the cavity contained PCE concentrations up to 14,000 ug/L.

A pump and treatment groundwater re-circulating system was installed in 1994 to mitigate contamination migration and flush residual contamination from the soil for capture and treatment. After two years of pump and treatment, there was no significant reduction in the contaminant concentrations in groundwater samples.

Cl-out bioremediation was initiated in 1996. The gravel backfill in the excavation UST cavity was used as an injection gallery. An active Cl-out bacteria population was maintained in the soil around the cavity by periodic Cl-out additions to the gravel backfill.

After less than one year of Cl-out bioremediation, the groundwater concentrations decreased by 90% to 99%. After two years of Cl-out bioremediation the PCE and other VOC levels in all monitoring wells decreased to less than the drinking water MCL. Figure 2 shows the cleanup trend in one of the monitoring wells.

The Kentucky Department for Environmental Protection
has given the property No Further Action (NFA) status. This status removes the environmental stigma from the property and restores its economic value.

Treatment of Groundwater Under Dry Cleaning Facility

Soil and groundwater contamination by chlorinated solvents was discovered at a former self-service dry cleaning facility in southwestern Ohio. The contamination had leached through the soil beneath the dry cleaners into the groundwater. The PCE concentrations in the groundwater were as high as 13,000 ppb. The typical anaerobic byproducts were also detected in lower concentrations, including TCE, 1,2-DCE, and vinyl chloride (190, 120, and 125 ppb, respectively).

The groundwater at the property is perched at the bedrock surface approximately 16 to 18 feet deep beneath the property. The groundwater flow direction is largely controlled by the fracture pattern in the bedrock. The groundwater contamination traveled through the fractures in bedrock in three directions from the property. The extent of groundwater contamination covered approximately one acre.

CI-out was introduced through one-inch diameter piezometers that were installed using direct push sampler. The small diameter injection points made it possible to install injection points inside the cleaners without disrupting the facility operations. Eight injection points were installed to cover the area of the groundwater plume.

The first CI-out inoculation on August 18, 2000 was a high dose of five drums to establish the CI-out microbe population within the treatment zone. A smaller inoculation, of three drums, was introduced after one and two months to maintain the CI-out microbial activity.

The monthly groundwater sampling results are summarized on Table 1. The monthly samplings show a continuous decrease in the PCE concentration from 13,000 to 650 ppb in three months. While there was an apparent slight increase in the TCE and DCE concentrations, vinyl chloride was not detected after the first inoculation. The table summarizes the data taken during the treatment period. Figure 3 demonstrates the extent of the VOC plume concentrations over time.

Cl-out bioremediation has achieved site-specific remediation goals for this site in less than three months, allowing the property to be marketed without environmental stigma. The total remediation and monitoring cost was less than $25,000. The CI-out bioremediation continues at this facility with the goal of reaching drinking water standards.

Accelerated Site Remediation

Cl-out bioremediation was used along with excavation to cost-effectively treat soil and groundwater contamination in less than two months. During a pre-acquisition due diligence of a chemical manufacturing facility, soil and groundwater contamination was found beneath a drum storage area. The contamination consisted of more than 20 volatile organic compounds. A primary contaminant was PCE, which was detected in groundwater as high as 470 ug/l. Although the contaminant concentrations were rela-
tively low, the concentrations exceeded applicable regulatory limits and impacted the potential property transaction.

To facilitate the property transaction, the drum storage pad was removed and the contaminated soil was excavated for off-site disposal. Cl-out bioremediation was then implemented in conjunction with air sparging and groundwater recirculation to accelerate the groundwater remediation. The combination of these technologies was used to accelerate the circulation of Cl-out microbes in the subsurface and to augment the microbial activity by boosting the dissolved oxygen concentration in the groundwater.

Remediation progress was monitored by analysis of samples from the groundwater circulation system. After less than one month, the PCE concentration decreased from 470 to 3.5 ug/l. The concentrations of its potential breakdown products, TCE, DCE, also decreased significantly. Overall, the concentrations of all contaminants were decreased by 90 to 99%. The groundwater sampling results are summarized in table 2.

Conclusions

These various field applications have proven that bioremediation with Cl-out can achieve fast and economical results. In many cases the environmental stigma was removed from the property, restoring the value within a few months. This technology can be used at a variety of different properties, including contaminated dry cleaning, industrial, or commercial sites. The accelerated approach may be used to complete site remediation much faster than traditional techniques and in a timeframe that facilitates a property transfer.

Mike Saul is Vice President and Michelle Broyles is a biologist, both with CL Solutions, Cincinnati, Ohio.
Bioremediation Plays 
Major Role on Two South Jersey Remedial Projects

By Gary R. Brown

Bioremediation has been successfully used on two South Jersey projects, one involving a petroleum products terminal, and another involving concrete products manufacturing facility. In addition to significant cost savings, use of bioremediation allowed for fast response, which was a critical element on both projects. Both projects were implemented by RT Environmental Services, a King of Prussia, Penn. environmental services firm.

Atlas Building Systems

Atlas Building Systems was a former concrete products manufacturing facility, in Voorhees, N.J. As required by the New Jersey Department of Environmental Protection, the facility was in the process of upgrading its stormwater management system, to include the construction of two large stormwater basins, in the rear of the facility. The facility manufactured large scale concrete components, including such items as bridge beams, large wall sections, and prefabricated floor slabs. Due to the large size of the manufactured items, the facility had a large yard area which could not be vegetated and needed to remain with a sand surface, so that the manufactured items could be allowed to cure and shipped in the future. Figure 1 shows a site layout.

Due to business considerations, the company announced a significant scaling back of operations which would result in job loss for most of the employees at the facility. The next day, a valve was found to be open on an oil tank in the manufacturing area and several thousands of gallons of oil traveled through the storm drainage system, and was present as a product layer in the lagoons. The release was immediately reported, and Clean Harbors, Inc., was retained to begin product recovery operations.

Because it was obvious that impacted soil was present around the edge of the surface impoundments and near the inlet pipe discharge area, bioremediation options began to be evaluated. In addition, even though the free product was being removed from the surface of the stormwater in the basins, there was concern that dissolved constituents could exceed applicable discharge limits. Stormwater discharge, once it leaves the facility, travels only several hundreds of feet through ditches and swales, and then flows into the Sturbridge Lakes system, considered to be a sensitive area with recreational uses.

As soon as free product removal was substantially complete, samples were obtained, which showed elevated concentrations of several number two fuel oil parameters, well in excess of applicable discharge limits. Concentrations of petroleum hydrocarbons were as high as 20-40 mg/l, in

Figure 1.

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excess of maximum discharge concentrations of 1 mg/l. Further, the size and the scale of the facility meant that it was imperative to proceed with remediation prior to the next rainfall event, as the volumes of stormwater produced at the facility and managed in the lagoons, would be too large to pump or berm.

The New Jersey Department of Environmental Protection case manager was contacted, and a representative of the Camden County Health Department was assigned to work with RT, due to the time sensitive nature of the project. Two tasks were deemed to be of critical importance:

- Excavate the impacted soils present in a "ring" around the edge of each basin, as well as the impacted soil areas below the inlet discharge pipe.
- Once that work was successfully completed, bioremediate by direct mixing of cultures and nutrients, the remaining impacted stormwater in the basins.

As excavation and field test kit equipment was mobilized to the site, technical review of the proposed bioremediation approach began. It was decided that the most time sensitive approach would be to place the impacted soils on a tarp and cover them, as bioremediation would need to occur using a landfarming technique over a several week period. Twenty to thirty cubic yards of impacted soil were excavated.

Direct mixing of cultures and nutrients into the stormwater then commenced. Due to the size of the basins, there was concern that mixing would not occur, so both pumps and a small boat were used to assure adequate distribution of the bioremediation agents over an hour or two. As rain was forecasted to occur at this point, as soon as the next day, it was critical to confirm via a certified laboratory that concentrations had fallen to below applicable discharge criteria. Although the field test kits were extremely helpful in determining the extent of soils to be remediated and demonstrating the effectiveness of the treatment as it occurred, only certified laboratory tests are official. A lab within ten miles of the project site agreed to accept samples late in the day and run them into evening hours, until all applicable discharge criteria were met.

Although there had been significant concentrations of several BTEX constituents in stormwater, all such constituents were now non-detect, and the TPH concentration was less than the 1 mg/l discharge criteria in the stormwater in both surface impoundments. With immediate time sensitive goals met, everyone breathed a sigh relief that the approximately 225,000 gallons of impacted stormwater were successfully treated on site, prior to the next rainfall event, when discharge of impacted stormwater would have been virtually unavoidable.

The following week, attention turned to the remediation of the impacted soils. Following approval by the New Jersey Department of Environmental Protection case manager, a landfarming area on plastic was setup and bioremediation agents were thoroughly mixed with soils in a des-
iganed area. Successful treatment of the impacted soils, to New Jersey Department of Environmental Protection Soil Remediation Criteria, was completed within three weeks.

Compared to conventional approaches, either involving temporary activated carbon treatment of the stormwater, or, conventional excavation removal and backfill of impacted soils, use of the bioremediation approach for both had estimated projects savings of $24,000. RT, in discussing options with plant management, had recommended bioremediation by explaining to the concrete products company that the technology was first understood and documented as a natural process during cleanup of the Prudhoe Bay Alaskan oil spill. The natural process could now be stimulated by adding cultures and nutrients, and would be perfect for a project such as this.

Although management was initially skeptical, when the bioremediation vendor was willing to offer a guarantee of no payment unless applicable criteria were achieved, the decision was easy. William Holub, General Manager of the facility commented, 'When the spill occurred, it was hard to believe what you were saying could actually be done. I'm still amazed at how well that all worked.'

Mr. Holub has traveled worldwide, and has a wealth of technical managerial experience in cement/concrete products operations. RTs demonstration to him that the technology was sound, cost effective and satisfied DEP, is a testament as to why bioremediation should receive early consideration on all similar petroleum release projects.

**Woodruff Energy**

The New Jersey Department of Environmental Protection has a pro-active program involving non-point source controls, which, in the case of large petroleum facilities, requires secondary containment around large tanks to make the containment area impervious. Woodruff Energy approached RT Environmental about the best option for upgrading of its secondary containment area at its facility in Bridgeton, N.J. The site, immediately adjacent to the Cohansy River, is a petroleum distribution facility going back to the very earliest parts of the 20th century. Woodruff Oil purchased the terminal from a major oil company, in 1959. 1.6 million gallons of aboveground petroleum storage capacity is present at the site.

Unexpected findings during the tank secondary containment upgrading project caused the need for emergency reporting to the New Jersey Department of Environmental Protection. A long abandoned buried municipal waste water treatment plant was found beneath a former product transfer pumping station being demolished as part of the project. Following the initial finding of floating oil product in old treatment pits, and because of concern that the waste water treatment system was still connected to the Cohansy River, caused a temporary shut-down in the secondary containment upgrading project.

Upon finding the buried wastewater treatment plant, immediate contacts were made with the City of Bridgeton as well as the Cumberland County Utilities Authority. It was identified that a municipal sewage treatment system has operated on the site from 1883 until 1927, and investigative work began immediately to determine the size and extent of the buried wastewater treatment tanks at the site. DEP expressed concern that product, or dissolved product, might be migrating to the River through unknown pipes or the former wastewater discharge system. Drawings showed a long discharge pipe to the middle of the river.

County utility officials were instrumental in completing an immediate record search an RT worked closely with Lynne Mitchell of the New Jersey Department of Environmental Protection Southern Field Office, as well as Tim Maguire, senior DEP hydrogeologist. We began to conduct an immediate multi-phase investigation to:

- Use data logging techniques to determine whether or not the wastewater vaults were hydraulically connected to the aquifer or river, which is tidal, and verify groundwater flow directions.
- Expediously determine the extent of impacted soils at the facility, as some areas of product saturated soils were found in the vicinity of the wastewater vaults, and some floating product was found in the vicinity of the oil pumping station.
- Large test trenches were also excavated parallel to the river, to determine and confirm that no pipelines existed which could convey product impacted groundwater to the river.
- Influent and effluent pipes to and from the wastewater treatment vaults, as well as other pipes, including product and old small diameter terra cotta pipes encountered during the excavation, were all drained and properly grouted so that there is no potential for further migration to the nearby river.

The New Jersey DEP considers the Cohansy River to be in need of environmental protection because of the presence of shell fish beds in the lower part of the river, in the Delaware estuary.

The entire project was conducted expeditiously using a team approach. RT and DEP shared investigation approaches and findings on a daily basis, following a DEP visit to the site by senior officials from the Southern Field Office. With winter approaching and the lining project shut down, the key concerns were:

- Completing the investigation project such that secondary containment lining could still be installed before cold weather arrived (HDPE selected for secondary containment cannot be installed in low temperature conditions).
- As the previous secondary containment earthen berms had to be opened for the entire project, all parties felt it important to proceed with the work expeditiously, so that the secondary containment could be put back in place.
- All expressed a desire to work closely together using a high degree of careful technical focus to reach common understandings on the specific goals and need for each investigation and remedial step, and to work quickly towards a solution.

The Project turned into a model of cooperation, meeting with full intent and spirit of the New Jersey ISRA/Brownfields law. Although many people are under the impression that the Brownfields Law only applies to contaminated, abandoned urban sites. ISRA revisions also
in the law actually allow DEP to adopt flexible and appropriate standards for petroleum release sites using a risk based corrective action process. RT worked closely together with DEP to use appropriate standards as localized areas around the waste water treatments vaults were investigated, taking into account that the area would be capped by the secondary containment liner. Also taken into the account were the investigation results, the site setting and migration potential.

Once it was demonstrated that all potential migration pathways of concern to the river had been located and successfully closed, Class II soil standards were found to be applicable, and remedial needs were focused on two particular "hot spot areas". These were expeditiously remediated by excavation and removal of soil. Soil was shipped to a regional bioremediation facility for treatment.

Engineering and investigation findings, as well as lab results and key technical findings, were forwarded to DEP by fax on a daily basis and investigation. Remediation of the entire tank farm/wastewater treatment area was completed in a short three weeks.

The availability of a local bioremediation option was very important to the overall project, from both a cost and schedule standpoint. The project involving the secondary containment installation only suffered minimal delay, because of the availability of the local bioremediation option. Trucks that were used to haul the petroleum impacted soils from the site were used to haul already clean bioremediated soils back to the site, eliminating double handling, maximizing remedial project productivity.

The extra remedial portion of the project, to include the free product removal, and excavations/removal/replacement of the petroleum impacted soils, had a total cost of $54,000. Savings on the project, attributed to the DEP’s use of flexible standards, as well as the use of bioremediation, totaled approximately $37,000, arrived at by comparing with the next most cost effective option.

Mr. Robert Woodruff, Sr., President of Woodruff Energy, commented that, "The level of cooperation was remarkable, in that daily investigation and remediation work could be planned and implemented with DEP oversight so as to be both focused and efficient. We thought that the costs for dealing with the treatment plant problem could have been much higher."

In all, more than 300 tons of soil were bioremediated. The project was a model of cooperation, and provides the assurance that Woodruff’s main tank farm facility has been through the investigation and remediation process so that areas under the liner system are no longer of environmental concern. Woodruff Energy is one of New Jersey’s ISRA/ Brownfields success stories, wherein fresh technical approaches including bioremediation and a high level of cooperation prove that environmental work can proceed quickly, efficiently and professionally.

**Conclusion**

RT Environmental Services has been implementing bioremediation on a wide variety of projects since 1993. Although bioremediation is not applicable to every type of potential petroleum release project, where it is technically appropriate and can be applied the advantages it can bring to a project are substantial. These include:

- Minimizing waste.
- Being able to respond to a release quickly, where surface water is involved.
- Having the opportunity for cost savings.
- Minimize project delays.
- Avoiding backfill costs.

Due to these attributes, RT recommends bioremediation receive first consideration when deciding how to deal with petroleum releases. Knowing how and when to implement the technology can lead to a high degree of project success, even when there is a big bump in the road.

Gary R. Brown, P.E. is with RT Environmental Services, King of Prussia, Penn.
Case Studies of Field Analysis by ASTM Method D5831

By Susan S. Sorini, John F. Schabron and Joseph F. Rovani, Jr.

Measurement of fuels and other petroleum products in soils is an important environmental activity. Field screening methods for this purpose are especially useful for defining boundaries of contamination and providing information on where samples should be taken for more expensive and time consuming laboratory analyses. Field screening methods can also result in cost savings for site excavations by minimizing their duration, and the incidence and costs of unnecessary removal of uncontaminated soils.

The quality of data generated by field and laboratory methods for analyzing soils for hydrocarbon contamination is dependent on the availability of information concerning the contaminant and the availability of a portion of the specific contaminant for standardization (Rhodes et al. 1996). Since the contaminant fuel is rarely available for calibration, the analytical results are dependant on the method and calibration material used. Thus, the various methods rarely provide comparable or truly accurate results. The common laboratory methods, which involve gas chromatographic separations, usually disregard the presence of materials heavier than diesel-range contaminants. Thus, used motor oil and heavy fuel oil contaminants are rarely reported. No two fuel analysis methods, laboratory or field, can be expected to give the same answer, because of the tremendous variations in fuels, the different principles of measurement, and the variation in soil samples, even if they are co-located. Typically, a laboratory reference method is agreed upon by the regulatory agency, the site owner, and the contractor. A field screening method is often used to select the points from which samples are collected for the laboratory analysis. It is important that the field method used does not provide false negative results. In addition, the manner in which the selected field screening method relates to the laboratory method should be understood. In planning remediation activities, field and laboratory method selection is very important.

Volatile petroleum products in soil, such as gasoline, can be screened in the field by simple headspace photoionization or flame ionization organic vapor analyzers (OVAs). However, mid-range distillates, such as diesel fuel, and heavier products are not effectively measured by these techniques and require a screening procedure that is sensitive to diesel-range and heavier petroleum products.

ASTM Method D 5831, Standard Test Method for Screening Fuels in Soils, provides such a procedure (ASTM 2000). This screening method has been tested in the laboratory and shown to recover mid-range and heavier petroleum products from soil (Schabron et al. 1995). Fuels containing aromatic compounds, such as diesel fuel, as well as other aromatic-containing hydrocarbon materials, such as motor oil, crude oil, and coal oil can be determined using the procedure. This screening method focuses on aromatic components in the contaminant, which are generally considered to be the more toxic components of petroleum hydrocarbon products with regard to both human health and the environment. This aspect of the method is particularly useful because, as diesel fuel in soil is subjected to bacterial degradation and weathering processes, the remaining fuel is more aromatic than the starting material and less volatile (Douglas et al. 1992).

The ASTM screening method uses low-toxicity chemicals and can be used to screen organic-rich soils. It is fast, taking about 10 minutes per sample; easy; and inexpensive to perform. The procedure calls for mixing a five-gram soil sample with approximately five grams of calcium oxide, which prevents interferences from moisture and humic materials in the soil (Schabron et al. 1995). The mixture is extracted with 50 milliliters of isopropyl alcohol (IPA) for three minutes. The resulting extract is filtered, and the ultraviolet (UV) absorbance of the extract is measured at 254 nm. If the contaminant fuel is available for calibration, the approximate concentration of fuel in the soil can be determined; if the fuel type is known, but a sample of the contaminant fuel is not available for calibration, an estimated concentration of fuel contamination in the soil can be calculated using an average response factor, which is given in the method; and if the nature of the contaminant fuel is not known, the UV absorbance value is used to indicate the presence or absence of contamination.

The Diesel Dog® soil test kit has been developed for field application of ASTM Method D 5831. The ASTM method can easily be performed in the field using the soil test kit. A 5-gram soil sample is weighed using a portable balance. After addition of calcium oxide, which is provided in moisture-proof, pre-weighed packets, and IPA, the mixture is stirred using a mechanical 12V extractor. Extraction is not performed manually, as is common for most field analysis methods, because manual agitation has been shown to be inefficient and non-repeatable (Schabron et al. 1995). The mechanical extractor has only glass, Teflon®, and stainless steel wetted parts and operates with a portable battery pack. A disposable syringe and filter are used to transfer the extract to a quartz cuvette, which is then inserted into a 12V portable photometer. The absorbance of the extract is measured at 254 nm, which provides direct
measurement of the aromatic components. The portable photometer also operates with the battery pack. The portable battery can be charged before being taken to the field and also has a cigarette lighter socket adapter for convenient use of the kit on the tailgate of a pickup truck.

The Diesel Dog soil test kit and ASTM Method D 5831 have been used at several sites to successfully screen fuel contamination in a variety of soils (Butler et al. 1997, Schabron et al. 1997, Sorini and Schabron 1996). In addition to these uses, the soil test kit and ASTM method have recently been used by ENSR Corporation and Wyoming Department of Environmental Quality (WYDEQ) at a number of field sites. These include an aged diesel-pond site in the U.S. Virgin Islands, a diesel-contaminated site in Georgia, a decades-old diesel and road tar site near Jackson, Wyo., and a filling station site in Sheridan, Wyo.

This article describes use of the Diesel Dog soil test kit and ASTM Method D 5831 at these sites, as well as their use at a private residence where a diesel spill caused the risk for potential contamination of a drinking water well. For each of these case studies, information is provided on how the method and soil test kit performed in the various applications.

**Case Studies**

**Aged Diesel-Pond Site**

ENSR Corporation of Acton, Mass. used a Diesel Dog soil test kit and ASTM Method D 5831 at a field site in the U.S. Virgin Islands. The site was a one-year-old pond impacted by diesel fuel. The soil in the area was very wet and sandy. Soil samples were screened in the field using the soil test kit and ASTM method. Soil samples were also analyzed in the laboratory using the Massachusetts Department of Environmental Protection extractable petroleum hydrocarbon (MADEP EPH) method (MADEP 1995). This method involves methylene chloride extraction of the soil in a Soxhlet apparatus. The solvent is removed from the soil extract, and the extract is re-dissolved in hexane prior to separation into aliphatic and aromatic fractions. The resulting extracts are analyzed using gas chromatography with flame ionization detection (GC-FID). Results from the field and laboratory tests are shown in Table 1.

As discussed, the results generated by the ASTM and MADEP EPH methods can be expected to vary because of the differences in measurement techniques. The concentration values listed in Table 1 for ASTM Method D 5831 are estimated values that were calculated using the response factor for diesel fuel that is given in the ASTM method. As shown in Table 1, the ASTM and MADEP EPH methods detected hydrocarbon contamination in all of the samples that were analyzed using both procedures. ASTM Method D 5831 results are higher than the MADEP EPH method results for five of these eight samples. For these samples, there may have been some heavier hydrocarbon materials (>C22) present, which the GC method would not detect. As is required of a screening method, no false negative results were generated by ASTM Method D 5831.

### Table 1. ASTM Method D 5831 Field Data and MADEP EPH. U.S. Virgin Islands Pond Site, mg/Kg.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ASTM Method D 5831</th>
<th>MADEP EPH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aliphatics (C1-C4)</td>
<td>Aromatics (C1-10)</td>
</tr>
</tbody>
</table>
| 1      | 2,200              | 110       | 10        | 120
| 2      | 3,500              | 12,600    | 100       | 12,700
| 3      | 3                   | 90        | 98        | 98
| 4      | 9,600              | 6,300     | 1,600     | 7,900
| 5      | 7,200              | 2,150     | 460       | 2,610
| 6      | 6,700              | 14,000    | 3,200     | 17,200
| 7      | 2,100              | 388<sup>3</sup> | 92<sup>3</sup> | 480<sup>3</sup>
| 8      | 1,400              | 284<sup>3</sup> | 41<sup>3</sup> | 325<sup>3</sup>
| 9      | 5,000              | 299<sup>3</sup> | 71<sup>3</sup> | 370<sup>3</sup>
| 10     | 1,200              | 43<sup>3</sup> | 13<sup>3</sup> | 56<sup>3</sup>

<sup>3</sup> estimated value

<table>
<thead>
<tr>
<th>Sample</th>
<th>ASTM Method D 5831</th>
<th>EPA Method 8015B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>130</td>
<td>&lt;12</td>
</tr>
<tr>
<td>2</td>
<td>92</td>
<td>&lt;12</td>
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<tr>
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<tr>
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<td>&lt;12</td>
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<tr>
<td>7</td>
<td>580</td>
<td>&lt;12</td>
</tr>
<tr>
<td>8</td>
<td>&lt;75&lt;sup&gt;3&lt;/sup&gt;</td>
<td>&lt;12</td>
</tr>
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<td>9</td>
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<td>&lt;12</td>
</tr>
<tr>
<td>17</td>
<td>20</td>
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</tr>
</tbody>
</table>

<sup>3</sup> estimated value

<sup>3</sup> The approximate quantitation limit (LOQ) The approximate quantitation limit (LOQ) for ASTM Method D 5831 for diesel fuel is the approximate quantitation limit (LOQ) for ASTM Method D 5831 for diesel fuel is 75 mg/Kg.

<sup>3</sup> duplicate value

<sup>3</sup> No analysis was performed.

**Diesel-Contaminated Site**

ENSR Corporation also used a Diesel Dog soil test kit and ASTM Method D 5831 at a site in Georgia contaminated with diesel fuel. The soil test kit and ASTM method were used to screen soil samples collected at drilling points. Soil samples were also analyzed in the laboratory using EPA Method 8015B (US EPA 1996), which involves analysis of methylene chloride extracts of the soil using GC-FID. The data that were generated by the analyses are shown in Table 2.

As discussed, differences in the results generated by the two methods can be expected because of the differences in measurement techniques. The concentration values listed in Table 2 for ASTM Method D 5831 are estimated values that were calculated using the response factor for diesel.
fuel that is given in the ASTM method.

The approximate quantitation limit (LOQ) of the ASTM method for diesel is 75 mg/Kg. The LOQ of EPA Method 8015B for analysis of the samples in this study was 12 mg/Kg. As shown in Table 2, of the 18 samples analyzed by both methods, five of the samples (6, 8, 11, 12, and 14) were determined to have contaminant concentrations less than the LOQs for both methods. Five other samples (2, 3, 9, 10, and 15) were determined to have estimated diesel concentrations slightly above the method LOQ using the soil test kit and below or just above the method LOQ using Method 8015B. For samples 1, 5, 13, and 18, EPA Method 8015B determined <12 mg/Kg of contaminant to be present, while ASTM Method D 5831 estimated concentrations of 130, 930, 1,700, and 120 mg/Kg, respectively, to be present in the samples. The laboratory method missed contamination in these four samples. Any weathering and bacterial degradation that occurred at the site may have degraded aliphatic portions of the contaminant leaving aromatic structures, which are tightly adsorbed to the soil matrix. IPA is a more powerful chromatographic solvent for displacing these adsorbed species than methylene chloride used in the laboratory method, resulting in a greater extraction efficiency (Snyder 1968 and Schabron et al. 1995). Three samples (4, 7, and 17) showed significant contamination by both methods, and for two of these, the ASTM method results were higher, which may also be due to the extraction efficiency of IPA.

The Diesel Dog soil test kit and ASTM Method D 5831 did not fail to detect contamination in any of the samples when compared to the data generated using EPA Method 8015B. The results from this study show that if ASTM Method D 5831 and the Diesel Dog soil test kit were used to guide an excavation at this site, the user could be confident that laboratory data generated by EPA Method 8015B would show that the cleanup had been performed completely and successfully.

Decades-Old Diesel and Road Tar Site

WYDEQ used ASTM Method D 5831 and a Diesel Dog soil test kit to guide excavation at a decades-old, fuel-contaminated site near Jackson, Wyo. The site was contaminated with diesel fuel and road oil from prior transportation department activities. The soil was a heavy wet clay. Under oversight by the WYDEQ, the engineering firm of Dames and Moore excavated about 6,000 cubic yards of soil, including about 2,000 cubic yards of overburden. Photoionization detector-based OVAs could not detect the contamination because the fuel had been weathered severely. A Diesel Dog soil test kit was used by a chemical engineer and a civil engineer to perform ASTM Method D 5831 on the tailgate of a pickup truck to provide rapid field data. According to the engineers, the soil test kit provided data within minutes. Soil samples were also analyzed in the laboratory using EPA Method 8015B. The laboratory data were obtained by a purge and trap sampling method for total volatile petroleum hydrocarbons (TVPH, C_6 - C_{10}) and by solvent extraction for total extractable petroleum hydrocarbons (TEPH, C_{11} - C_{28}).

Two sets of data were generated using ASTM Method D 5831. Estimated concentrations of diesel fuel in the samples were calculated using the response factor for diesel (209 mg/L/AU) that is given in the method. The other contaminant at the site was road tar. The location of the site in Wyoming suggests that the road tar came from the highly aromatic Recluse, Wyo. oil. As a result, the concentration of oil in the samples was estimated using the response factor for coal oil (58.7 mg/L/AU), which corresponds to a highly aromatic oil.

Data generated using ASTM Method D 5831 and the laboratory gas chromatography method are provided in Table 3. As shown in Table 3, the results of ASTM Method D 5831 for samples 1-6 are significantly higher than those determined by the laboratory method, regardless of whether the response factor for diesel or coal oil is used. This result is not surprising for several reasons. First, the contamination at the site occurred decades ago, and extensive weathering and bacterial degradation have occurred. Aliphatic portions of the contaminant have been degraded by bacterial action, leaving the most persistent portion of the contaminants, the aromatic structures, which are tightly adsorbed to the soil matrix. These can have aromatic structures >C_{22}, which would not be detected by the gas chromatography method. Also, as mentioned, IPA is a more powerful chromatographic solvent for displacing these adsorbed species than methylene chloride, resulting in a greater extraction efficiency. A similar trend was observed in a study in which spiked soils were weathered artificially (Schabron et al. 1995) and in a study involving use of the ASTM method and soil test kit at a railroad site where diesel fuel had been released during railroad maintenance activities for a period spanning approximately 80 years (Schabron et al. 1997).

Table 3. ASTM Method D 5831 ASTM Method D 5831 Field Data and EPA Method 8015B Decades-Old Diesel and Road Tar Site in Jackson, Wyoming, mg/Kg

<table>
<thead>
<tr>
<th>Sample</th>
<th>ASTM Method D 5831</th>
<th>EPA Method 8015B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As Diesel&lt;sup&gt;a&lt;/sup&gt;</td>
<td>As Coal Oil&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>1</td>
<td>490</td>
<td>130</td>
</tr>
<tr>
<td>2</td>
<td>150</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>610</td>
<td>160</td>
</tr>
<tr>
<td>4</td>
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<td>6</td>
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<td>81</td>
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<tr>
<td>7</td>
<td>6,000</td>
<td>1,600</td>
</tr>
<tr>
<td>8</td>
<td>7,200</td>
<td>1,900</td>
</tr>
</tbody>
</table>

<sup>a</sup> Approximate quantitation limit is 75 mg/Kg as diesel fuel.
<sup>b</sup> Approximate quantitation limit is 20 mg/Kg as coal oil.
<sup>c</sup> Total volatile petroleum hydrocarbons, C_6 - C_{10}.
<sup>d</sup> Total extractable petroleum hydrocarbons, C_{11} - C_{28}.

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When samples 7 and 8 (Table 3) were analyzed using the soil test kit in the field, the results showed significant contamination requiring action. The field screening had identified a "hot spot" area within two days before site activities were to be terminated. The highly contaminated area was successfully excavated using ASTM Method D 5831 and the Diesel Dog soil test kit data. Data confirming the "hot spot" of contamination and successful excavation of the area were obtained from laboratory analysis more than a week after the site cleanup effort had ended.

Filling Station Site

WYDEQ conducted an excavation project involving removal and disposal of 9,200 cubic yards of contaminated soil from a filling station site in Sheridan, Wyo. The contamination was the result of two recent gasoline spills and several smaller older spills. Four soil samples were taken from the excavation, two from the bottom and two from the sidewalls. It was assumed that the sidewall samples were not contaminated. The results from ASTM Method D 5831 analyses of the soil samples from the sidewalls showed no contamination. The samples from the bottom of the excavation contained estimated concentrations of 180 and 220 mg/Kg diesel fuel according to the Diesel Dog soil test kit results. The corresponding laboratory GC analysis results were 32.5 and 66.7 mg/Kg, respectively, for gasoline to diesel range fuels. The results that were generated using the ASTM method are higher than the laboratory GC results, which as discussed, is to be expected for weathered fuel contamination.

Bus Barn Site

WYDEQ conducted an excavation of 2,670 cubic yards of contaminated soil from a transportation depot facility. The ground was contaminated by leakage from an underground storage tank, which had been removed in 1989. Following the excavation, two soil samples were collected from a sidewall and analyzed at the site using ASTM Method D 5831 and the Diesel Dog soil test kit. No contamination was detected in the samples, and follow up laboratory analysis was deemed to be unnecessary.

Emergency Response for a Diesel Spill

A contractor was hired at a private residence to steam clean the carpets and upholstery. The steam cleaning equipment was in a large trailer, which contained a diesel engine. After the contractor had completed the job, which took several hours, a diesel spill on the driveway and in the soil and gravel along the side of the driveway was discovered. The exact perimeter of the spill was difficult to determine because a lawn sprinkler had wetted the area before the spill was discovered. The homeowner was concerned because the spill was only about 15 feet from his drinking water well. The contractor estimated the spill to be 5 to 10 gallons. Although there was little chance that this amount of diesel could penetrate the soil to the aquifer 150 feet below, there was the potential that the well and aquifer could become contaminated via the well casing. If the outside of the casing and the surrounding bedrock had not been sealed with concrete at the time that the well was drilled, surface water could flow down the outside of the well casing into the aquifer below.

ASTM Method D 5831 and the Diesel Dog soil test kit were used at the residence to determine the concentration of diesel contamination and the extent of the excavation needed to remediate the spill site to proper cleanup standards. The WYDEQ regulatory level of 100 mg/Kg was used as the remediation standard. A semicircle at the edge of the driveway about 5 feet wide and 2 feet deep was excavated. Soil was sampled from three equally spaced locations around the inside perimeter of the excavated area. The soil samples were analyzed using the soil test kit on the tailgate of a Jeep®. The estimated concentrations of diesel in the samples, which are shown in Table 4, were determined using the response factor for diesel that is given in the ASTM method. The data listed in Table 4 for samples 1 and 2 show that the first excavation was sufficient to collect the spilled diesel that absorbed into the soil around the driveway. However, as shown in Table 4, the third sample, which was collected from under the concrete slab of the driveway, contained a very high concentration of diesel. As a result, additional excavation was performed, and when this was completed, two soil samples were collected from under the driveway and analyzed using the soil test kit. The estimated concentrations of diesel in these samples, which fall below the regulatory level of 100 mg/Kg, are shown in Table 4. With these results, the homeowner and contractor were confident that the spill had been cleaned up to proper levels, and the possibility of aquifer and well contamination had been avoided.

Summary

ASTM Method D 5831, Standard Test Method for Screening Fuels in Soils, provides an easy, fast, and inexpensive screening method for fuel contamination in soil. The Diesel Dog soil test kit was developed for field application of ASTM Method D 5831 for use in site evaluations, cleanup activities, etc. This article describes use of the Diesel Dog soil test kit and ASTM Method D 5831 at a

| Table 4. ASTM Method D 5831 Field Data for a Diesel Spill Emergency Response Site |
|-----------------------------------|------------------|
| Sample                           | mg/Kg as Diesel |
| First Excavation                 |                 |
| 1 (8" deep)                      | 51              |
| 2 (4" deep)                      | 98              |
| 3 (1" behind concrete edge)      | 20,000          |
| Second Excavation                |                 |
| 4 (8" behind concrete edge)      | 73              |
| 5 (8" behind concrete edge)      | 69              |

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A variety of fuel-contaminated sites. For each of the case studies, information is provided on how the method and soil test kit performed. In general, ASTM Method D 5831 and the Diesel Dog soil test kit provided higher values than the laboratory methods (MADEP EPH method and EPA Method 8015B). This is due to the differences in measurement techniques. In many cases, the screening method detected higher contaminant concentrations because of its sensitivity to the more aromatic components in the contaminant and because of the extraction efficiency of IPA. Of particular importance is that the ASTM method and soil test kit did not provide false negative results for any of the samples described in the case studies.

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Horizontal Wells for Subsurface Remediation

By Louis B. Fournier

After nearly 15 years of development and over 1,000 projects, directionally-drilled horizontal wells are finally being accepted as a viable and important tool for subsurface remediation. Far from being simply an alternative to vertical wells and trenches for site access, horizontal wells offer significant technical benefits that are not possible using these alternatives. Moreover, while initially considered by the environmental industry to be simply an expensive drilling alternative for getting under buildings and paved areas, horizontal wells have been found to reduce total site remediation project costs by 50% or more, depending upon remediation technology deployed.

Easier Site Access and Less Disruption

It is true that an important aspect of horizontal wells is that they can be installed under buildings and paved areas. They can also be installed on sites to avoid disruption during remediation project operation and to "get under" refineries, chemical plants, terminals, railyards, and other facilities where the exact locations of pipes, sewer lines, utilities, tanks (especially those associated with historic operations) within the installation are not well known, thereby making the installation of vertical wells and trenches difficult. Horizontal biosparge wells, in particular, are easily installed below all possible subsurface structures. Horizontal wells may be one-ended (Figure 1) or two-ended (Figure 2).

Chicago Highway Project

Horizontal wells are also important where above-ground activities make the installation of conventional processes impossible. For example, a pipeline leak in Chicaco resulted in petroleum hydrocarbons under a major six-lane highway. In the area of the release, a large office building was on one side of the highway and a large shopping center on the other side. The installation of vertical wells was impossible without major adverse impacts on area operations, including closure of the highway during construction. Operation and maintenance activities on the surface would have been nearly impossible without grave safety concerns. To address this situation, directionally drilled horizontal wells were drilled from the basement of the office building through a sump pump, across the highway, and then up to a 6-foot diameter grassy circle in the parking lot of the shopping center.

JFK Airport Remediation

At JFK Airport on Long Island (Figure 3), subsurface releases of jet fuel around gate areas and runways from historic operations at the International Arrivals Building resulted in soil and groundwater contamination which was cleaned up to NYDEC regulatory requirements using a combination of horizontal soil vapor extraction (HSVE) and horizontal air sparge (HAS) wells. The areal extent of contamination was 70 acres and the volume of contaminated groundwater was estimated to be 2.3 million gallons. Approximately 47,000 lbs. of volatile organic compounds (VOCs) were removed by the HSVE system over 18 months of operation. During the same time period, approximately 352,000 lbs of petroleum hydrocarbons in the saturated and unsaturated zones were treated by in situ biodegradation. There were no significant adverse impacts on or shut-downs of airport facility operations. Indeed, most operations personnel and airline passengers were unaware that remediation was being conducted over a large area of the site. Areas of the Delta Terminal and the former Eastern Airlines Terminal have also been addressed at JFK Airport using directionally-drilled horizontal wells.

Free Product Remediation

JFK Airport is the first site to fully document that horizontal biosparge wells can clean up separate-phase-hydrocarbons (i.e., "free product") without the need for additional free product recovery equipment or procedures. Up to 2' of actual free product was treated by in situ biodegradation. In fact, careful data analysis indicated that approximately 90% of total contaminants were treated biologically with the balance being removed as vapors by the HSVE system.

New York Pipeline Project

Since then, other sites have shown similar results. At a pipeline site in New York, horizontal biosparge wells placed around the release are preventing the migration of separate-phase and dissolved gasoline contaminants. Horizontal biosparge wells in the center of the plume are addressing the source area where several feet of gasoline are present. This case history is but one example of two major findings about horizontal sparge wells:

- They are highly effective at preventing the spread of contaminants to down-gradient receptors or off-site.
- They can be used to treat source area contamination to
regulatory standards without supplemental treatment steps, even with large amounts of petroleum free product present.

Large DOI Treats Free Product
A major reason that horizontal air sparge and biosparging wells can treat free product (as well as dissolved and sorbed contaminants) is the large distance-of-influence (DOI) typically obtained, usually 50’ to 120’ on each side of the horizontal well. This is much larger than the radius-of-influence (ROI) typically obtained with vertical biosparging wells, commonly 10’ to 25’ (Figures 4-7).

This very large DOI is thought to be due to the lack of soil disruption above the screened interval as compared with a vertical well which is drilled from the surface directly downward. Soil disruption increases soil permeability around the vertical well which in turn reduces the observed ROI for vertical wells.

This effect is completely absent with horizontal wells. Horizontal biosparging or air sparge wells, for example, are always designed for a minimum DOI of 50’ even though DOIs of 75’ and 120’ (based on observed air bubbling in monitoring wells and/or increased oxygen concentration in groundwater) have been observed.

Treatment of MTBE and Other Recalcitrant Contaminants
The very large DOIs obtained with horizontal air sparge and biosparging wells results in their being very effective for addressing recalcitrant organic contaminants such as MTBE and chlorinated solvents. A large DOI creates a wide aerobically-active biozone. Contaminants may reside in this zone for months to years. Hence, biodegradation processes which are slow to occur in laboratory tests and with vertical wells occur easily with horizontal wells. With MTBE, in particular, it is thought that the long residence time allows first BTEX and then MTBE to be biodegraded sequentially. Losses of volatiles via physical removal processes may also be contributing to observed decreases in contaminant concentrations although contaminant levels at the surface and in on-site buildings in the neighborhood of horizontal wells are generally below detection limits. For many contaminants, it is not the strength of the oxidant which is important, but rather the duration of bio-oxidation treatment.

Treatment of Chlorinated Solvent Contaminants
Horizontal air sparge and biosparging wells (as well as horizontal soil vapor extraction wells) are ideally suited for treatment of chlorinated solvent plumes. In all cases, there are at least three contaminant removal processes operational concurrently: hydrolysis, in situ biodegradation and physical volatilization. The relative rate of one of these removal/treatment processes versus the other two is a function of many site-specific characteristics and parameters.

In situ aerobic biodegradation processes can be either direct or co-metabolic. TCE daughter products (cis- and trans- dichloroethylene and vinyl chloride) are rapidly removed by direct aerobic bioreaction using horizontal sparge wells. TCE and PCE are slowly removed. The presence of a suitable co-contaminant such as toluene or the addition of secondary substrates such as methane, ethane, propane, butane, and others promote co-metabolic, aerobic biodegradation processes which are extremely effective for treating TCE and PCE. At one site, a system of 18 dual-phase vertical extraction wells was expected to require 30 years of operation to meet cleanup requirements for toluene, TCE, and daughter-products. Discontinuation of the operation of the dual-phase extraction system and substitution of three directionally-drilled, 400-foot long biosparging wells resulted in site cleanup to regulatory standards in three months.
Engineering Design of Horizontal Well Systems

Unlike vertical well screens (where soil particle sizing is commonly used as a criteria), horizontal well screens must be designed using fluid dynamics computer programs in order to achieve the air (or vacuum) distribution required (which is usually linearity of distribution). Water recovery or injection wells are less critical, but still need to be designed properly. Air-based systems are extremely difficult to design properly, especially if they are long and deep. Fortunately, there are vendors with appropriate computer design programs that can produce well designs and remediation equipment designs which have been demonstrated to work exactly as required on numerous projects. The use of appropriate and proven computer design programs to engineer well screens and associated equipment cannot be stressed enough. Too many horizontal wells and well systems have failed because inexperienced and non-knowledgeable personnel have provided their designs.

Horizontal Well vs. Vertical Well Project Costs

Comparison

Properly designed horizontal well systems can dramatically reduce over-all project costs. If the total cost of a vertical well pump-and-treat system is assumed to have a baseline cost of 100%, for example, the use of horizontal wells instead of vertical wells with the same pump-and-treat system will generally result in a total project cost of 80 to 90% (i.e., a 10 to 20% cost savings). If water treatment can be eliminated by use of horizontal wells and an air sparge/soil vapor extraction system, the total project cost will be about 50% of the baseline vertical well case, a 50% cost savings. If horizontal biopurge wells can be used, the total project cost (compared to the baseline vertical well case) will be about 20%, a savings of about 80% of total project costs. These are average values. A more detailed cost comparison must be performed according to the remediation technology deployed.

The comparison of costs of horizontal wells versus vertical wells, must be based on site-specific information such as type of soil present, the depth to groundwater, the depth of the vertical and horizontal wells below grade, the type(s) of contaminants present, etc.

However, if we assume a sandy aquifer with water table at say 10’ below grade, petroleum hydrocarbon contami-
nants, and a horizontal screen depth of approximately 20' below the water table.

**Biosparging**

If the remediation technology is "biosparging," a comparison ofHWs vs. VWs is as follows:

- Assume that a single biosparge well with 400' of screen, 100' of header (i.e., the distance from the blower to the screened interval), and 100' of "tail" (i.e., the distance from the screened interval to the distal end of the well) is installed. At a MINIMUM, the distance-of-influence (DOI) of this well will be 50' on each side of the well plus a half-circle around each end of the well (at the water table). The total area which will be treated will be 47,854 sq. ft.

Note: We always use 50' as a MINIMUM DOI as the design basis for such wells since we have never seen less than this value for a properly designed horizontal biosparge or air sparge well. At one project, we observed 72' DOI on each side of the well and on another we observed 120' DOI on each side of the well (both in sandy aquifers with the wells 10-20' below the water table).

- A vertical biosparge well on this same site will likely have a radius-of-influence (ROI) at the water table of about 15'. The treatment area at the water table will be 707 sq. ft. However, this treatment area must be reduced by approximately 10% since the vertical treatment areas must be over-lapped to cover the entire site. Thus, the effective treatment area of the vertical well will be approximately 636 sq. ft.

Note: In the literature and in our personal experience, the ROI of biosparge and air sparge wells typically ranges from perhaps 8' to 25'. We have used 15' as an average for ROI in sandy aquifers for the assumed project.

- Dividing the treatment area of the horizontal well (47,854 sq. ft.) by the treatment area of the vertical well (636 sq. ft.)

**Figure 4.** A vertical sparge well typically has a radius-of-influence of 10 to 20 feet at the water table, much smaller than the distance-of-influence obtained with a horizontal biosparge well. Note the area covered at the water table by a vertical well with an ROI of 15 feet as compared with the area treated at the water table with a horizontal sparge well with a 50-foot DOI. The same scale is used for both.

**Figure 5.** Approximately 75 vertical sparge wells would be required to treat the same area of water table that can be treated using a single horizontal biosparge well with a 50-foot distance-of-influence (DOI). Based on air bubbling in monitoring wells and dissolved oxygen increases in water samples, DOIs for horizontal biosparge wells have ranged from 50 to 120 feet (at the water table).

**Figure 6.** Industry practice is to report the ROI distance of vertical sparge wells as measured at the water table, typically 10 to 20 feet. Below the water table, the ROI diminishes to just a few inches at the well screen due to the effects of the air buoyancy and increased permeability of soil due to disturbance of soil during drilling for vertical well installation.
gives 75, the number of vertical wells that it would take to treat the same area. That is, it would take 75 vertical biosparging wells to treat the same area as the single horizontal well.

Note: We recognize that there are many consultants who might not put in this number of wells, but the assumption is that we are trying to treat the same area at the water table.

• Assume that the cost of drilling the horizontal well is $150 per foot (if you would rather assume another number, go ahead). Then the cost of drilling the horizontal well will be $150 x 600 = $90,000.

Note: We usually use $100 per foot as a good drilling number but then exclude mobilization/demobilization, well materials cost, engineering design costs, etc. On advice of others who have reviewed this, we have increased this to $150 per foot to better reflect the total costs that might be associated or incurred with a horizontal well project for the assumed example. It is possible that costs may be lower or higher than this value. You can add additional mobilization/demobilization, engineering, well materials costs, or whatever else you wish to this cost, or decrease it if you wish for a more accurate calculation.

• Now assume that the cost of installation of a vertical well is $5,000. (We have seen costs ranging from $2,500 to $10,000 per well. If you have a better number, use it.) Then the cost of the vertical wells will be 75 x $5,000 = $375,000. You can add cost of trenching to connect vertical well points, well materials, labor for making connections, etc. to this base cost. These additive costs will be far greater than the additive costs for the horizontal well.

• The horizon cost is $90,000 versus $375,000 for the vertical wells, a difference of $285,000. That is, the horizontal well installation cost is only 24% of the cost of the equivalent vertical well system (i.e., to treat the same area at the site).

• Now, consider the blower cost. The single horizontal well will require only 1 blower. Let’s say that the cost of that blower PACKAGE (i.e., blower, heat exchange, control system, etc.) will be $25,000.

• For vertical wells, it is not generally possible to place more than 7 vertical wells on a blower and to have them operate with any degree of uniform air distribution. Even with only 7 wells, it is virtually IMPOSSIBLE to keep a multiple-vertical-well system "balanced". Usually, if a system is manifoldered, air will flow through one or two vertical wells only and there will be no air flowing through the other wells. BUT, for the sake of comparison, let’s assume that 7 vertical well can be placed on a single blower. With 75 wells, essentially 11 blowers will be required (i.e., one blower will have only 5 vertical wells instead of 7). At a cost of $25,000 per blower, the total cost of blowers for the vertical well system will be $11 x $25,000 = $275,000.

Note: We have been performing a fair number of "forensics studies" of operating vertical and horizontal well air sparg er and biosparging systems. In most of these projects, a number of wells are manifoldered together to one blower. Where this is the case, we have NEVER found more than 1/3 of the manifoldered wells to be actually operational. That is, some are blowing air while the others are completely dead, even with proper flow control equipment present and an operator testifying that the system is "balanced". We recognize that there is a great deal of "belief" that multiple wells manifoldered to a blower can be kept balanced. We even know of at least one site where 35 vertical wells are manifoldered to a single blower and the major consultant "swears" that the system is always balanced. We don’t believe it!

• Comparing blower cost only, the horizontal well will require a single blower at a cost of $25,000 while the vertical well system will require 11 blowers at a cost of $275,000. The horizontal well blowers will cost only 9% of the cost of the vertical well blowers.

• In total, using the above numbers, the cost of the horizontal well system (i.e., blower plus well installation) will be $90,000 + $25,000 = $115,000 plus additives + O & M. The cost of the vertical well system will be $375,000 + $275,000 = $650,000 + additives + O & M. Thus, the "raw cost" of the horizontal well system will be only 17.7% of the cost of the vertical well system.

• The cost of additives and maintenance for the vertical well system will be much greater than the cost of additives and maintenance for the horizontal well system. When everything is totaled, the total project cost for the horizontal...
well system will be about 10% of the cost of the performance equivalent vertical well biosparge system.

**Air Sparging and Soil Vapor Extraction**

If the remediation technology is air sparging and soil vapor extraction (AS/SVE), then:

- There will be essentially twice as many wells (i.e., half for AS and half for SVE).
- The AS blower will be more costly in that more air must be produced (i.e., we design horizontal air sparge wells to operate at 1.0 SCFM per foot of well screen and horizontal biosparge wells to operate at 0.5 SCFM per foot of screen, half the volumetric output. SVE wells must operate above the AS output, typically 1.5 to 2.0 SCFM per foot of screen).
- In general, the cost of a horizontal well air sparge/soil vapor extraction system will be about double the cost given above for the horizontal biosparge well system. Similarly, the cost of a vertical well air sparge/soil vapor extraction system will be about double the cost given above for the vertical well biosparge well system. Hence, as a rough number, the cost of the AS/SVE horizontal well system will be $230,000 versus $1,300,000 for the vertical well AS/SVE system. The percent comparison remains the same.

**Pump-and-Treat**

Now suppose you want to compare the cost of a horizontal well groundwater pump-and-treat system with a vertical well groundwater pump-and-treat system. In reality, what you need to compare is the water production of the vertical well versus the water production of the vertical well in order to calculate the number of vertical wells required to produce the same water quantity. But, you may not know this comparison because neither horizontal nor vertical wells have been installed at a site.

- In the absence of valid, site-specific information, a rough approximation of the cost comparison can be obtained based on "well screen in the ground". For example, a horizontal well with a 400'-long screened interval will, obviously have 400' of well screen in the ground. Let's assume that a vertical well would have 2' of screen in the ground (use any number you like). If we can assume as a rough approximation that the volumetric flow rate of water into the well per foot of screen is the same for each system, then it will require 400 divided by 2 = 200 vertical wells to produce the same amount of water as the single horizontal well.
- If the same costs as given above are used for comparison purposes, the horizontal well will cost $90,000 to install while the vertical wells will cost 200 x $5,000 = $1,000,000 to install. That is, the horizontal well system will cost only 9% of the vertical well system!
- Now, assume for the sake of comparison that each of the wells will need a water pump costing say $5,000). The horizontal well will need only one pump at a cost of $5,000. The vertical wells will need 200 pumps costing $5,000 each for a total of $1,000,000. (In fact, a larger pump may be required for the horizontal well than for the vertical wells, but we'll use the present numbers for now.)

- Then the over-all project cost of the horizontal well system will be $90,000 + $5,000 = $95,000 + additives + O&M. The total cost of the vertical well system will be $1,000,000 + $1,000,000 = $2,000,000 + additives + O & M. And, once again, the maintenance and additives cost of the vertical well system will be far greater than for the horizontal well system. On a "well installation + equipment" cost basis, alone, the horizontal well system will be less than 5% of the cost of the vertical well system.

**Directional Drillers**

Although there are over 8,000 directional drillers in the United States, only about a dozen are sufficiently experienced and knowledgeable to provide the well installation, well development, and other services required for a successful project. Many others either have or are planning to enter the market. Similarly, there are less than a handful of engineering design firms that can produce an acceptable well and equipment design for horizontal wells. For short wells, they are sometimes successful; for longer wells, they almost always fail. Unfortunately, most do not have the performance test equipment and skills necessary to even know that they have failed.

**Migration Control**

While horizontal wells can be used to treat both source areas and plumes, a significant application is to protect against off-site migration and/or to address contaminants which have already migrated off-site. One important tool in this application is the use of horizontal SVE wells. Depending on stratigraphy, soil composition, depth, diameter, and other factors, a properly engineered horizontal well can achieve DOLs of 150' for vapor collection. Along property lines, horizontal biosparge wells provide a "line in the sand" beyond which contamination may not migrate.

Horizontal wells will not address any and all situations. For example, if the site is highly stratified with multiple contaminated sand and clay layers, a trench or multilevel vertical well system may be preferable. Conversely, however, if contamination exists in only one or two sand layers, including in a confined aquifer, the selective use of horizontal wells may be beneficial.

**Horizontal Well Materials**

Virtually all possible well materials have been used with horizontal wells including polyvinyl chloride (PVC), fiberglass, mild steel, stainless steel, and high-density polyethylene (HDPE). Of these, for a variety of reasons, HDPE has emerged as the front-runner. It is relatively inexpensive, has high durability to most groundwater contaminants, and is less expensive to install than heavier well materials. Moreover, it does not have the brittleness and breakage problems typically associated with PVC.
NGWA Interest Group

In recognition of the current and future importance of horizontal wells in site remediation, water production, site assessment, and other applications, the National Groundwater Association (NGWA) has a Horizontal Well Interest Group. This group publishes a newsletter called "Horizontal News" which is free upon request to NGWA members. The NGWA has also established a web site which contains, among other things, a 1500-reference bibliography on horizontal wells and projects, a posting of past newsletters, and other information. Lastly, the NGWA has established a free list-server available to both members and non-members for posting of questions related to horizontal wells and their applications. In addition, more information is available on the websites: www.angelfire.com/biz/horizontalwells and www.integrityengg.com.

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Sediments Forum

USEPAs Forum on Managing Contaminated Sediments at Hazardous Waste Sites: Summary of Policy Discussions

By Richard J. Wenning

For scientists, environmental managers, and environmental policy-makers in the United States engaged in the investigation or remediation of contaminated sediments, four reports reflect their call for focused and concerted actions to address contaminated sediments in our nation's waterways.

First was USEPAs 1998 Report to Congress on the incidence and severity of sediment contamination in the United States. Prepared in conjunction with both the National Oceanic and Atmospheric Administration (NOAA) and the Army Corps of Engineers, the Agency estimated that approximately 96 watersheds containing over one billion cubic yards of contaminated sediments warranted some level of assessment and management (Figure 1). More than two-thirds of these watersheds, representing nearly 15% of the nation's lake acreage and 5% of its river miles, already had fish consumption advisories in place.

Less than one year later, USEPA published its Contaminated Sediment Management Strategy. The strategy described the Agency's work plan for actions needed to bring about assessment and reduction of the ecological and human health risks posed by contaminated sediments. The strategy established four goals: source control and prevention of further sediment contamination; reduction in the volume of in-place contamination; use of environmentally sound remedial measures; and, promotion of scientifically sound sediment management tools for pollution prevention, source control, remediation, and dredged

Figure 1. Probable areas of concern identified by the EPA in the 1998 Report to Congress on contaminated sediments in the continental U.S. Source: The Incidence and Severity of Sediment Contamination in Surface Waters of the U.S. (September 1997).

Figure 2. The Presidential/Congressional Commission on Risk Assessment and Risk Management (1997) framework for environmental health risk management.

Figure 3. The NRC (2001) Technical Committee's refinement of the Presidential/Congressional (1997) framework for application to the risk management of PCB-contaminated sediments.
material management.

At nearly the same time, the National Research Council (NRC) reported on the concerns of technical experts that currently available technologies for cleanup of contaminated sediments in U.S. ports, harbors, and waterways were capable of addressing only the less severe aspects of the problem. New technologies and innovative programs were needed to address potentially highly toxic sediments in a manner that would minimize or reduce human exposures and injuries to aquatic resources.

The fourth, and latest, report in this series was issued by the NRC earlier this year. Its Risk Management Strategy for PCB-Contaminated Sediments summarized the current state of knowledge of human health and ecological impacts posed by PCB contaminated sediments and provided recommendations for a wide-range of investigation and research activities as part of a strategy to reduce the risks.

The NRC Committee selected the framework developed by the Presidential/Congressional Commission on Risk Assessment and Risk Management (Figure 2), and refined the framework for application to managing the risks posed by PCB-contaminated sediments, potential remediation options, and risks that remain when remediation is complete (Figure 3).

The NRC report made strong recommendations in support of use of a risk-based decision framework. This included an emphasis on the use of sound risk management principles, extending beyond the more traditional risk assessment approach. The NRC Committee also acknowledged that all remedial options have advantages and disadvantages and, in particular, that dredging cannot be expected to remove all contaminants. The NRC report recommended that all risks of implementation for each remedial option under consideration should be considered, including risks occurring both during and after the implementation phase of the remedy. Finally, the NRC Committee recommended that the net environmental benefit of each remedial option should be considered and compared.

In the context of the Superfund program, where the fate of the majority of contaminated sediment problems rest, the USEPA faces, perhaps, its most complex environmental challenge to date. Using the Agency’s estimates for the fraction of material deemed sufficiently toxic to fish and wildlife to require removal or isolation, treatment, and disposal, the projected costs to the Superfund program for cleanup are enormous. Many experts have concluded that the magnitude of the problem could be on the order of several billions of dollars, or more. Using USEPA (1998) estimate of 1.2 billion cubic yards of contaminated sediment and a mean dredging cost up to $250 per cubic yard, nationwide remediation costs could exceed $5 trillion in the United States.

What is the appropriate approach to investigation, assessment, and remediation of contaminated sediments? Who should be involved? What are the important technical, regulatory, and public policy requirements? What level of investigation and assessment is required to define appropriate remedies? What are appropriate remedies? And, how should they be evaluated for short- and long-term effectiveness?

USEPA Sediment Forum

To address these and other difficult questions, the USEPA Office of Emergency and Remedial Response (OERR) hosted an open technical forum for discussion of five key aspects of investigation and remediation of contaminated sediments at hazardous waste sites. The five aspects are community involvement, hazard assessment, site characterization, remedial effectiveness, and risk management.

The purpose of the forum was to facilitate an open exchange of information and viewpoints among experts involved in the cleanup of contaminated sediments. Thirty panelists with recognized expertise in each of the five disciplines led discussions involving nearly 400 participants representing industry, state and federal environmental agencies, engineering companies, health consulting firms, academic institutions, environmental groups, and Native American interests.

The forum provided participants with a unique opportunity to explore the important science and policy issues currently under consideration by the Agency for making site-specific risk management decisions. With USEPA staff in the Superfund Program office currently engaged in drafting guidance on assessment methods for contaminated sediment at hazardous waste sites, forum participants could highlight key technical considerations, the lessons learned, and coax further considerations by the Agency on several difficult issues. The new guidance is anticipated in draft form in early 2002.

The specific aims of the USEPA sediment management forum were to:

• Provide a forum for stakeholders to express opinions on USEPA program policies and guidance that address sediment remediation;
• Identify the key site information and data that should be collected and evaluated to make informed site-specific cleanup decisions;
• Identify issues that need to be resolved, additional data that needs to be gathered and evaluated, and research that needs to be performed; and,
• Share information and the lessons learned as a result of managing sites involving contaminated sediments.

Five Aspects of Contaminated Sediment Management

Accordingly, the forum was organized to facilitate the sharing of information and discussion of key technical issues across five important aspects:

Community involvement. Nearly twenty years of CERCLA program experience has taught both the regulated and regulatory communities that community involvement is a critical element in the decision-making process at hazardous waste sites. Citizens groups, Native American tribes, and other special interest groups are increasingly recognized as important stakeholders with special interests often misunderstood or inadequately considered during both the investigation and remediation stages.

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Effects on human health and ecological resources. For risk managers and the public to understand the scientific issues that support effective remedial solutions, there remains an urgent need for clear communication and education across several disciplinary boundaries. The CERCLA program has taught us that scientifically defensible, site-specific risk assessment and environmental analysis still founder when discussions turn to scientific and engineering uncertainties. And often at times, these efforts fail to adequately address the questions important to stakeholders.

Site characterization. Site-specific investigations, assessments, and remediation of contaminated waterways imply the development of site-specific conceptual site (or, sediment) models to guide the entire process. But, the investigation methods and technologies that should be employed to understand site-specific conditions are often viewed by the public and by regulatory agencies as time consuming or, at worst, as delay-tactics by PRPs. At issue is defining the appropriate breadth and level of detail required of site-specific investigations to characterize both retrospective and prospective temporal and spatial trends of the contamination.

Remedy effectiveness. Even in a perfect world where technical experts agree on both the environmental impacts and site characteristics, there would remain considerable disagreements over the efficacy of different remediation technologies and appropriate methods for evaluation of the long-term effectiveness of selected remediation options. Furthermore, ongoing releases from uncontrolled or non-point sources, natural disasters (e.g., severe flooding), and incomplete or inadequate site characterization can undermine the long-term success of the chosen remedy.

Risk management frameworks. The various risk management frameworks emerging among different state and federal agencies, industry groups, and academic institutions require convergence, at least on the basic principles. Achieving consensus among these different stakeholder groups may be the first, and largest, challenge among all concerned parties.

Forum Themes: Community Involvement

Involvement of the local community in the investigation, assessment, and decision-making process has become an increasingly important activity for both potential responsible parties and regulatory agencies. A public involvement plan that incorporates the concerns of environmental organizations and other special interest groups, and particularly those of Native Americans, is increasingly recognized by experts as an essential early step in contaminated sediment management strategies throughout the country.

Among the two essential elements of community involvement program, project advisement and education, education may be the most critical component. According to Larry McShea from Alcoa, Inc., the complex nature of contaminated sediment issues requires that community advisory panels get involved early in the process to allow adequate time to gain an understanding of the technical and policy issues before important decisions are made. The significant complexities that all stakeholders must grapple with include the evaluation and selection of sediment management options, assessment of human exposures and adverse health effects, ecological risk concerns, and societal issues related to use restrictions on public access waterways.

Jennifer Sutter from Oregon DEQ concurred, noting the success of Technical Advisory Panels (TAPS) comprised of local environmental and engineering experts; local, state, and federal agencies; and the interested public. TAPS can provide a link between the public and oversight agencies and also provided a forum for independent peer-review of regulatory and PRP activities, thereby building confidence and trust among the various stakeholder groups. She also noted the value of reaching out to local interest groups to provide updates at their meetings and on their turf, which tended to reach more people and were more appreciated than the typical formal public meetings.

The community involvement approach used by USEPA Region 6 for the Calcasieu Estuary in Louisiana represents another approach to community involvement. Among the four key components of USEPA Region 6 approach, involvement of local government early in a local leadership role may be most important. Other components include the establishment of outreach activities such as local advertising of significant events and findings, workshops, and opening of local information offices. The release of environmental data as it becomes available and ahead of formal reports, which may be months away, builds trust. And the last component, frequent communication with potentially responsible parties to facilitate open communication on difficult issues, was a common theme throughout the discussion on community involvement.

The concept of community extends not just to affected municipalities, cities, and towns but also to sensitive populations and special interest groups. According to Tom Nelson, environmental specialist representing the Omi Nation in Wisconsin, the management of contaminated waterways in Indian Country poses special challenges often ignored or inadequately addressed by decision-makers. Tribal societies differ across the country, defying generalizations and requiring tribe-specific considerations during the assessment phase and when promoting the final remedy. Incorporating their concerns and needs likely will continue to pose a challenge to environmental agencies and other stakeholders.

Forum Themes: Assessing Human Health and Ecological Risks

Consensus is building among technical experts and regulatory authorities that risk-based approaches to investigation and remediation of contaminated sediments should be favored for their cost-effectiveness and ability to prioritize public health and ecological concerns. Difficulties arise, however, over the uncertainties and often considerable conservatism required to fill data gaps in both human health and ecological risk assessments.

The age-old argument between reliance on best-case or worst-case assessments of current and prospective expo-
sures and health risks remains at the heart of this debate. Most experts would concur with decisions that err on the side of safety. At issue is the appropriate magnitude of that margin of safety and the degree of resolution required in the assessment to distinguish that margin.

The importance of developing more realistic approaches for characterizing the extent of exposure at contaminated sediment sites was emphasized in presentations by Natalie Wilson, from N.D. Wilson and Associates, and Dr. Todd Bridges, from the U.S. Army Corps of Engineers. The application of unnecessarily simplistic approaches to characterizing the punctuated nature of exposure to mobile receptors like fish often leads to erroneous conclusions about the true risks to ecological and human receptors. The example presented by Dr. Bridges for the NY Bight emphasized that assumptions that constrain the movement of highly mobile receptors to the confines of relatively small contaminated sites results in highly exaggerated assessments and generates uncertainties that significantly undermine confidence in the decision-making process.

The weight-of-evidence approach advocated by Dr. Charles Menzie, from MenzieCura & Associates, highlights one mechanism for early agreement among stakeholders regarding the magnitude of that inevitable margin of safety. The framework used in Massachusetts relies on reaching a consensus among stakeholders on appropriate assessment and measurement endpoints in waterway assessments. Dr. Lucinda Jacobs at Exponent concurs, adding that advancements in risk assessment such as the use of a tiered assessment approach and quantitative uncertainty analysis can significantly reduce uncertainty and minimize data gaps.

Nonetheless, as Dr. Frank Bolen from the University of Connecticut cautions, weight-of-evidence approaches, as well as other site characterization methods, still require careful consideration of the level of precision necessary to answer the question of environmental fate, impacts on ecosystems, and the subsequent scope of the remediation effort.

Another approach, which deviates from risk-based assessment methods, involves the use of numerical sediment quality guidelines and sediment toxicity testing to predict the probability of adverse effects to bottom-dwelling benthos. According to Dr. Chris Ingersoll from USGS, a commitment to large data collection efforts involving matching sediment chemistry and laboratory toxicity analyses can effectively reduce uncertainties regarding characterization of the extent of adverse ecological impact of contaminated sediment. Additionally, the generation of site-specific data to evaluate the applicability of nationwide or regional-based sediment quality guidelines could be a cost-effective means for making sediment management decisions.

However, there is considerable debate among experts on the accuracy and appropriate use of numerical criteria, and particularly on whether sediment quality guidelines are effective at predicting sediment toxicity and adverse ecological effects across different marine and freshwater environments. Dr. Alan Burton, from Wright State University, noted that experience thus far indicates that there can be considerable differences between the nature and magnitude of adverse effects on indicator species observed in the laboratory and the effects observed under actual field experimental conditions. Furthermore, Dr. Robert Engler, from the U.S. Army Corps of Engineers, observed that numbers alone cannot be used as benchmarks and cleanup goals because they address only the effects side of the risk paradigm without consideration of causality or the extent of exposure.

Much as the NRC (2001) report indicated, technical and policy discussions on sediment risk assessment methods, the utility of numerical criteria, and the role that both of these tools should play in decision-making at contaminated sediment sites remain unresolved and capable of provoking considerable debate among experts.

**Forum Themes: Site Characterization**

If each Indian tribe is unique and different, then certainly no two waterways are alike either. There is broad consensus that site characterization methods must be site-specific and tailored to explore and evaluate a waterways unique environmental and biological conditions. In fact, several sets of unique conditions may be evident in larger waterways such as the Hudson River or Fox River, each requiring their separate and focused investigations and assessments.

At present, the debate concerning appropriate site characterization methods swings widely between those experts who seek to generalize waterway behavior into a basic model framework, and those experts who seek to establish key measurement indicators and advocate implementation of a full suite of characterization tools. One issue in this debate is the importance of distinguishing between site characterization efforts that generate need-to-know information from those that produce nice-to-know information. Risk-based decision-making, at a minimum, requires site-specific environmental data. And regardless of the focus, site characterization must adequately address the spatial, temporal, and exposure aspects of a risk-based management paradigm, and provide sufficient quantification of the uncertainties associated with the chosen characterization methods to inform decision-makers of possible limitations and data gaps.

The importance of problem formulation early in the investigation process was evident to all forum participants. Regardless of the approach, Dr. John Connolly, from Quantitative Environment Analysis, advocates the application of the scientific method to establish and ask the important questions in a hypothesis-testing framework. But, there are some difficulties with regard to the practical aspects of this approach to site characterization beyond mass balance modeling and source control investigations.

Source investigation curing site characterization is one area of general agreement among experts. Site characterization must address ongoing sources because the success of any future remediation activities by risk managers requires no net inputs to the affected environment. Bioavailability and contaminant flux also must be well
understood. Food web transfers and pathways of human exposure must be evaluated and the linkage to contaminated sediment conditions confirmed at the site. Sediment stability, particularly the risk of remobilization during severe natural climatic events (e.g., flooding), must be evaluated.

Forum Themes: Remedy Effectiveness
For contaminated sediments requiring remediation, remedy selection often hinges on the decision whether to dredge sediments, promote natural recovery of the affected waterway, or cap contaminated materials in place. Considerations of long- and short-term remedy effectiveness are important issues that stakeholders should consider for all management options. A brief review of waterway projects completed to date suggests that these three options do not provide the level of environmental protection and finality required by all stakeholders.

Representing the considerable expertise of the Army Corps of Engineers on this subject, Dr. Michael Palermo observed that the current debate about dredging contaminated sediments focuses on concerns regarding short-term potentially negative impacts on wildlife and human health. For example, while capping may impose lower short-term environmental impacts than dredging, severe natural climatic events and unintentional man-made disturbances that violate the in situ barrier may pose considerable longer-term risks.

And, in the case of dredging, downstream losses of contaminated material and their short-term impacts during the removal process need to be balanced against the long-term capability for the ecology of the affected waterway to recover.

The third remediation option, monitored natural recovery (formerly referred to as natural attenuation, or by its sharpest critics as the no action alternative), is gaining serious consideration as a reasonable approach for some contaminants. But as James Chapman, from USEPA Region 5, and Dr. Victor Magar, from Battelle, observed in their case studies, more research is needed to improve understanding of natural processes and to advance the lessons learned at several successful project sites such as Lake Hartwell, S.C. to other sites. In some cases, the reasons why natural processes fail to fully attenuate contamination under conditions that appear ideal for natural processes are not completely understood. It is on this basis, according to Emily Green, representing the Sierra Club, that activities that appear to reflect the no-action alternative are unsatisfactory.

There is general agreement with Dr. Palermo’s five criteria for evaluating short- and long-term effectiveness of capping and dredging/disposal options. The time to achieve remediation goals must be considered. Contaminant releases during and following construction activities must be evaluated to understand whether the remedy has the potential to do more harm than good. The permanence of the remedy must be forecast under several reasonable and worst-case scenarios. The high costs typi-cally associated with the majority of contaminated sediment projects does not tolerate remedy failure. And, finally, the implementation of the remedy approach must be practicable to the specific areas of concern at the site.

Forum Themes: Risk Management Frameworks
Several contaminated sediment management frameworks in various stages of development are available from a wide range of stakeholders at the present time. Managing the risks posed by contaminated sediments at hazardous waste sites are likely to remain elusive long after the technical issues related to site characterization, risk assessment methods, and remediation technologies have been resolved.

Four common themes are evident among the different proposed frameworks. Risk management should address the need for source control, strive to reduce in-place contamination, use scientifically sound investigation, assessment, and remediation methods, and involve implementation of environmentally sound management options. A successful framework should involve all concerned stakeholders and provide each with a forum to express opinions, concerns, and share ideas. The framework may have a national set of guiding principles, but must be flexible and tailored to waterway-specific conditions and solutions.

Echoing some of the eleven recommendations specified in NRCs (2001) risk management strategy for PCB-contam-
inated sediments, forum experts agreed that a site-specific risk management framework should comprehensively evaluate the broad range of risks posed by the occurrence of contaminants in sediments and any proposed remedial action. Management options should be risk-based. Source control measures are relevant to the remedial decision-making process. There should be no presumptive remedies or undue focus on a single preferred remedial option. Engineering and other less intrusive options are likely to be necessary to address the range of human health and ecological concerns at a site. A similar set of what could be called "guiding principles" is described in the detailed decision-making framework proposed by the Sediment Management Work Group (Figure 4). The framework and several supporting technical documents can be found on their web site at www.smwg.org.

Finally, the overall framework for managing risks will likely extend far beyond the project lifetime because of the need for long-term monitoring to evaluate the effectiveness of the management approach and to ensure adequate, continuous protection of public health and the environment. The scope and duration of post-remediation monitoring will be a function of the level of site-specific uncertainty between the occurrence of contamination and its direct link to measurable adverse ecological effects and human health impacts.

Closing Considerations
A synopsis of the meeting and copies of the presentations given by invited panelists will be made available by USEPA OERR on the internet. Documents will appear on the Superfund web site at www.epa.gov/superfund/ before the end of this summer.

The next steps in the technical dialogue process initiated by the Superfund Sediment Team within USEPA's Office of Emergency and Remedial Response will likely include regional workshops around the country to further explore the issues in each of the five focus areas. Special technical forums are likely to explore topics such as sediment transport, ecotoxicology, bioavailability, fish consumption surveys, remediation technologies, and specific sediment contaminants. New technical and policy documents anticipated from USEPA over the next year will likely include guidance on sediment remediation, a risk-based policy framework for contaminated sediments, and a proposed contaminated sediment research plan.

There also is an expectation among forum participants for more frequent dialogue, information exchange and joint research activities among technical experts from industry, academia, and regulatory agencies; between different state and federal regulatory agencies; and with citizen groups, environmental organizations, and other special interest stakeholders.

Technical and policy changes are underway to address the calls for action heralded in the four USEPA and NRC reports published within the past four years. Over the next few years we are likely to see more integration and greater consensus among diverse technical and policy experts on appropriate sediment characterization methods, site-spe-
Eye on ECOS
State Environmental Agency Contributions to Enforcement and Compliance
By Bill Kucharski

One of the primary obligations of a state regulatory agency is to ensure that the rules and regulations that define the agency are enforced. Environmental rules and regulations have one ultimate goal: to improve the quality of our environment. However, the number of enforcement actions taken against a regulated group is one of the primary indicators used by the U.S. EPA and many citizen groups to define how effectively an environmental regulatory agency or environmental program is being managed. Both the number of actions taken against violators of environmental rules and the dollars in fines and penalties imposed upon those violators are used to define an effective operation. This has always seemed to me to be a backward approach to defining a successful program. That is, the higher the fines and the more enforcement actions an agency imposes on industry, the better the program is believed to be. If improvement in the environmental quality of this country is the ultimate goal, then significant compliance with an environmental program should mean that the violations and fines should be less, not more than in a poor compliance situation. The inverse appears to be used as a good program criterion however. In many groups, a low number of penalties or violations is viewed only as poor enforcement, not good compliance. This belief is based upon the premise that no regulated entity will comply with the law unless they are hounded by enforcement. Given this mindset in many people, how enforcement activities are counted, reported and described is important in the perception battle of state environmental agencies.

There are obviously two primary levels of environmental enforcement in this country; federal and state. Some states, such as California have delegated environmental decision making and enforcement activities to county and local authorities, but the majority of enforcement activities in most states are handled by the appropriate state agency. There have been several recent reports issued by special interest groups that have slammed state environmental enforcement activities. Claims have been made that states have slacked off on enforcement issues and are letting the regulated communities run free. The only way to "save" the nation’s environment, it is claimed, is to have the federal EPA do the majority of the enforcement. This belief is in some ways supported by EPA reports on enforcement. However, most, if not all, state environmental leaders feel as I do; that more penalties and violations show that a program is in trouble, not that it is succeeding.

Because the states believe that the weak enforcement label is wrong and misleading, ECOS recently conducted a thorough enforcement study with the states. The remainder of this column will provide some of the salient facts provided by "Report to Congress: State Environmental Agency Contributions to Enforcement and Compliance".

Report to Congress
As of 1999, ECOS reports that about 70% of those federal environmental authorities that could be delegated to the states have been so delegated (for example, RCRA authority, NPDES, SDWA etc). While most people focus on the federal government’s role in environmental law, the states have not been silent. It is reported that of the environmental statutes passed by state legislatures, fully 70% of these acts have nothing to do with federal requirements. In short, the states are increasingly taking control of environmental issues within their boundaries. This includes additional environmental controls and innovative enforcement. This is important when one examines federal reports concerning state enforcement activities. When federal agencies report actions, they report only those activities directly associated with federal laws and authorities. To size this problem, in 1997, states passed over 700 environmental bills which, when the 70% state factor is added, results in approximately 500 state only laws passed in that year alone. This transfers into a very large data lapse, especially when it is realized that whatever enforcement is required within these state only laws, none is reported by the EPA.

As was stated in the first part of this article, most state environmental officials prefer to focus activities on improving environmental compliance than to obtaining major penalty collections (a favorite EPA tactic). That does not mean that states will not seek large penalties when appropriate, it means that a few regulated entities are so recalcitrant as to require such treatment. That is also not to imply that the very large settlement/penalties set by the EPA are wrong or counter productive. The EPA should be the "gorilla in the closet" because some industrial entities will only respond to the stick.

Since 1994, EPA has had an Office of Enforcement and Compliance Assurance (OECA). This group carries out the enforcement activities for the EPA. OECA prepares a report annually called the "OECA Accomplishments Report". These reports summarize and document the priorities and the accomplishments of the group for the past
year. These reports attribute approximately 69 to 80% of all environmental enforcement activity to the states. In fact, the actual numbers exceed these claims. As we have discussed earlier, one of the main state positions is that numbers of certain activities, such as enforcement actions, are not, in and of themselves, effective measures of program strength. However, if federal agencies or citizen groups are going to judge a program by using these numbers, they ought to be at least accurate. Following are excerpts and details from the ECOS report.

"The States report that they regulated over 1.75 million sites in 1999. The States inspected these sites over 501,000 times and made over 449,000 additional compliance evaluations in 1999. The states found over 25,700 significant violations, but only 15,500 were considered significant by EPA. The States received over 88,400 citizen complaints in 1999 (data from 33 States). Once all the problems were found, the States issued over 67,200 notices of violations and warning letters, and undertook many kinds of enforcement actions detailed in the report. In all, States conducted about 90% of all enforcement actions taken by both the States and EPA. The States collected almost $92 M in penalties in 1999" (Pg 13)

There are other salient facts detailed in the report. The level of compliance from certain types of enforcement actions tells a very interesting story. States reported that facility compliance resulted 76% of the time oral warnings were issued. When a Notice of Violation was issued, compliance rose to over 81%. Consent decrees resulted in an 83% compliance result while unilateral agency orders resulted in compliance 86% of the time. In short, if compliance is the goal, enforcement actions appear to obtain that result without massive fines or criminal charges, most of the time. The numbers associated with these compliance results are not consistently reported by non state agencies however. For example, states issue "significant non-compliance" violation reports. These reports reflect state standards of what is "significant". The state numbers vary considerably from the numbers reported by the EPA. This single definitional discrepancy is one of many reporting differences ECOS described.

The report states "Most State programs report a higher number of significant violations under state definition than under federal definition. Across all State programs for which comparable data were provided, States reported over 112,000 significant violations, compared to just over 60,700 Significant Non-Compliances by EPA. There are many reasons why States have counted more significant violations than EPA. States may be more stringent enforcers than some observers may have thought. States may have a lower threshold for what constitutes a significant violation. States may count violations at smaller sources. Even when the State and federal definitions match, the databases kept at the State program level and at EPA may not (match)." (pg 28). Of major note in this regard is this reported fact: "ECOS found that 80% of the States had experienced significant and pervasive data discrepancies between their state data and the same data as it appears in an EPA database."

In addition to significant non-compliance issues, states and federal reporting have other differences. States use oral warnings, Notice of Violations (NOV) and other lower level enforcement tools more frequently than federal agencies do. For example, states issued over 36,700 NOVs in 1999. EPA enforcement reports do not count these as enforcement efforts. An additional 37,000 oral warnings and warning letters were additionally issued by the states in 1999. Not counting the lower levels of enforcement action results in a large discrepancy. Specifically, for 1999, EPA counted 11,720 nationwide enforcement actions, crediting the states with 70% of these (8,200) while state records show over 90,899 actions were taken in this time period. The states accounted for over 90% of these actions (81,000). So, the EPA, in 1999 for example, credited and reported only about 10% of actual state enforcement actions.

The entire second section of the ECOS report contained comments on the EPA databases utilized for collected state data. AFS, PCS, RCRIS and SDWIS data bases were examined and commented upon. Other issues reviewed included the differences in definitions and the differences in data criteria that contribute to state and federal number mismatches.

Summary
In summary, the ECCS report on state/federal reporting differences associated with enforcement activities shows that one must be very careful about using select data if the goal is to inform people of what is actually happening in the environment. If one chooses carefully which data to report, as in any field, very different conclusions can be drawn. States can come off as "soft" on enforcement if incomplete data are reviewed. The states are not only bearing the overwhelming burden of environmental enforcement, the states are also in the forefront of environmental innovation and thereby, are improving the quality of our environment. The public should be made aware of the facts. I hope the ECOS report will help achieve that goal.

The full text of the report may be retrieved from the ECOS web page; www.ecos.org.

Acknowledgement
I want to thank Steve Brown, deputy executive director of ECOS and the primary author of "Report to Congress: State Environmental Agency Contributions to Enforcement and Compliance" for permission to quote the facts in this article.

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Bioremediation can be defined in many different ways. It could be the active degradation, or passive removal, or concentration of environmental pollutants by a biological system. Or it could be degradation by a specific enzyme in a microbial or plant cell. A plant system might increase the rate of degradation due to the unique characteristics of the rhizosphere. Bioremediation might involve the concentration, or deposition of inorganic pollutants in the rhizosphere. It could also involve plants as the agents of passive movement of pollutants out of soil and into the atmosphere. There are undoubtedly still other ways of looking at or defining bioremediation.

Since its first description, bioremediation has been subdivided into more specific and descriptive sub-areas which have separate names. The flow chart below indicates these various 'branches' of the bioremediation tree. The most common division is between microbial and phytoremediation. In the former case, microorganisms, bacteria, actinomycetes and fungi are the active organisms in the remediation process. In phytoremediation, typically trees are the active organism. However, from the flow chart you will note that other plants and microorganisms have been used in bioremediation.

Plants and trees interact with soil to produce an area around the roots called the rhizosphere. This is an area of high microbial activity, lower pH, increased organic matter, higher carbon dioxide and lower water and nutrient content. Particularly because of increased microbial activity, this area also contributes a unique environment, conducive to the break down of organic compounds. Because plants are constantly taking up water, the rhizosphere is an area where concentration of metals and organic compounds occurs. Once in the rhizosphere, inorganic and organic compounds, including metals, may be deposited, taken up or broken down by plants.

Active degradation of contaminants involves enzymes, or metabolic pathways, which accommodate the pollutant. The plant or microorganism may use the pollutant as a source of nutrients, carbon, nitrogen, phosphorus etc., as a source of energy, or both. Common short-lived insecticides and herbicides are broken down and used in such a manner. Nitrates can be removed from water under anaerobic conditions by a process called denitrification. During this process nitrate is used as an electron acceptor and thus the organism is using the nitrate in energy production.

Passive removal could be uptake along with water and release into the atmosphere by transpiration. Gases dissolved in water may be taken up by plants, transported up the plant system and released into the atmosphere during transpiration. On the other hand, one might simply wish to have trees remove water from soil to prevent it and associated pollutants from moving into or out of the area. Passive removal can also take place in the rhizosphere. This could be by concentration, or by concentration and precipitation. If a plant can be found which takes up the contaminant, then the plant can be grown and the pollutant "harvested" along with the plant. If the pollutant is a metal, the plant material can be burned and the metal recovered. If the pollutant is a heavy metal and it is precipitated in the rhizosphere, then the plant, roots and surrounding soil may need to be "harvested".

Versatility is the rule. It was once thought that microorganisms were omnipotent. That is, that they could and would break down any organic compound. This was particularly true of soil microorganisms since there are a tremendous variety of different types of microorganism, aerobes, anaerobes, heterotrophes, autotropes, bacteria, actinomycetes, fungi, etc. in soil. However, some complex organic compounds are highly resistant to degradation. Of most concern are manmade compounds, which are toxic. There are also some natural organic compounds, such as humus, which are also resistant to decomposition. These compounds are generally seen to be beneficial.

In addition to complexity, concentration is a problem. If the pollutant is too concentrated, it may interfere with biological activity. This could be direct interference as in toxicity or indirect as in the creation of a high osmotic potential. On the other hand, if the concentration is very low, there may not be enough of the pollutant present to sustain the population of degraders.

For situations where the pollutant is highly concentrated, and thus interfering with degradation, then dilution may be necessary. If the pollutant is soluble in water, then adding water may be sufficient. This would also work if the problem is osmotic. If the pollutant is insoluble, then soil or some inert additive might be needed as a diluent. This of course presents the additional problem of creating more polluted material.

It might be noted that water-soluble compounds are usually more easily decomposed than are water insoluble.
materials. In some cases, the addition of a surfactant will bring the pollutant into solution and result in an increased rate of decomposition.

In situations where the pollutant concentration is low, the decomposition process may be slow. Addition of organic matter to maintain a high microbial population may help in these situations. On the other hand, it may be better to allow additional time to permit the natural decomposition process to proceed. This would only be a viable process where the pollutant was not able to move out of the polluted site.

For microorganisms, surviving the competition with other microorganisms is problematic. If the microorganism needs the pollutant to live and it is at low concentration, then maintaining a large population of the microorganism so that rapid degradation takes place will be hard. If the microorganism degrades the pollutant along with other needed substrates, the question then becomes - will there be enough of the needed substrate present to allow for degradation of the pollutant?

Survival is the name of the game. If a plant or microbial species is not adapted to a location or an environment, will it survive to do its remediation work? If the answer is yes, the question then becomes for how long? For plants, particularly trees, adaptability to a variety of environmental conditions may be great. However, if trees are to be used to control water movement in an area, where the water contains some salt or is brackish, will the trees live? One might also ask which variety of tree will grow best.

One approach, which has been tried, is to find or develop a microorganism capable of degrading the pollutant in question. This microorganism can be grown in large numbers and added to the soil to effect remediation. This will only work if the organism survives. Often these organisms do not survive, meaning that new batches must be added to soil frequently.

Bioremediation using any type of organism is a valuable remediation tool. It has many advantages including the fact that often it is carried out in situ and thus involves minimal disturbance to the site. In addition, microorganisms and plant roots can explore every recess of soil and thus carry out a more complete remediation.

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Forensics

Identifying and Differentiating High and Low Temperature Tars at Contaminated Sites


Tars derived from petroleum, coal, or mixtures thereof are an important class of environmental contaminants that can be encountered, for example, in former manufactured gas plants (MGP), tar processing facilities, and wood treatment operations. The environmental forensic investigator is often asked to identify the nature and source of tars or tar-derived contaminants at or near sites where current or legacy operations handled tar products. Thus, an understanding of tar chemistry is important knowledge for the environmental forensic investigator confronted with such issues.

The chemical signature of tar depends largely on the composition of feedstock (petroleum or coal), carbonization temperature, air and moisture content and condensation kinetics. The additive effect of these variables imprints the produced tar with a source signature. This article discusses the mechanisms of tar formation with a focus on the influence of temperature on tar composition.

Low Temperature Coal Tars

Low temperature carbonization of coal was used for four primary purposes. They include the generation of 1) liquid fuels, 2) solid domestic fuel of a smokeless and easily ignited nature, 3) solid industrial fuel for pulverized furnaces designed for byproduct recovery, and 4) blending agents other than semi-bituminous coal for the generation of metallurgical coke from high-volatile coals. Unlike Europe, the U.S. exhibited a minimal demand for the products of low temperature carbonization through the 1920s due to the cheap supply of petroleum and, later, natural gas. In addition, this process experienced heat transfer difficulties through the coal bed that impacted its commercial viability. Despite these difficulties, low temperature coal combustion sites arose periodically in the U.S. with the emergence of promising technological innovations, elevated energy costs and national security initiatives.

Low temperature carbonization involved the heating of coal in the absence of air. Coal beds heated to approximately 100°C released moisture and occluded gases. With the exception of carbon dioxide emissions, little change in the coal occurred until the coal bed temperatures exceeded 300°C to 400°C. While the specific temperature of thermal decomposition depended largely on the type of coal, gas coals generally began degrading around 370°C. Low temperature tars were generally formed as the temperature increased from 370°C to 550°C or 700°C, depending on the carbonization technology.

Using the technology available before 1945, the general products of low temperature carbonization included a low yield of gas enriched in hydrocarbons; a high yield of light tar; a low yield of ammonia, cyanide and naphthalene; a high yield of hydrogen sulfide; and a semi-coke with 10 to 20% of the original carbon content. The temperature for these processes is critical; starting too high results in tar with high yields of ammonia and cyanide, and starting too low results in tar with high gas yields. Furthermore, a higher yield of tar is obtained as the temperature is raised from 370°C to 550°C or 700°C.

Figure 1. Conceptual model describing the manufacture of coke, gas and tar (adapted from Morgan, 1926).

a. Stages of coal carbonization, coke formation and associated oven temperature gradients.

b. Formation and movement of tar and gases during coal carbonization.

Retort Wall
Coke of variable volatile composition
Uncarbonized coal

Retort Wall
Coke of variable volatile composition
Plastic Envelope
Uncarbonized coal
15% volatile matter. The low temperature tar contained saturated and unsaturated hydrocarbons usually with hydrocarbon side chains. It also contained variable quantities of other sulfur and nitrogen compounds. Little secondary decomposition occurred under low temperature environments; consequently, the volatile matter was not subjected to the conditions that enriched the parent (unsubstantiated) polycyclic aromatic hydrocarbons (PAH) in high temperature coal tar. By contrast, the yield of tar acids in low temperature tar exceeded that of high temperature tar by 4 to 8 times.

High Temperature Coal Tars
The industrial production of coal tar peaked between 1910 and 1930 with the byproduct coke oven and horizontal retorts. In both of these systems, coal was placed in a sealed chamber, and heat was applied through the chamber wall. The temperature applied to the chamber walls ranged from approximately 900°C to 1100°C for coke ovens and horizontal retorts, respectively. However, the internal temperatures of the coal bed were not uniform (Figure 1a).

When the temperature of the coal exceeded approximately 370°C, the volatile constituents (gas and tar) began moving away from the larger molecular weight material (coke) via the path of least resistance. As stated previously, the actual temperature of gas and tar formation depended largely on the type of coal. The continued application of heat caused the coal to fuse and soften; thereby, forming a thin (<1") plastic zone or envelope within the coal bed. This plastic layer dramatically retarded the passage of heat. The temperature on either side of the plastic enve-

lopes differed by as much as 300°C. Consequently, high temperatures (>800°C) were often required to force the carbonization process to completion in less than 24 hours.

Studies of the carbonization process suggested that the majority of the volatiles emerged from the hot side of the plastic layer (Figure 1b, pathway B) because 1) more volatiles were formed on the hot side of the coal bed (Figure 1b, A > C), 2) the pathway offered less resistance and/or 3) the temperatures on the cool side of the plastic layer condensed the volatiles (Figure 1b, D). The passage of volatiles through the coke bed caused the formation of characteristic degassing pores (Figure 2). In addition, this passage through the hot coke bed promoted the secondary decomposition of the volatiles and enrichment of parent PAH.

As the temperature of the coal rose above about 500°C to 600°C, the release of gas continued, but the amount of tar decreased. As the heating progressed above 700°C, a large quantity of hydrogen evolved. When the temperature rose above 800°C, the coal volatiles were largely driven off and only the coke remained. Gas manufacturers often drove the temperature higher because hydrogen-enriched gas used as a bulking agent was generated economically up to 1100°C without completely destroying the value of the coke.

Environmental Forensic Interpretation
The thermal signatures of low and high temperature tars can be identified in the residuals of each respective process. Low temperature signatures include high relative concentrations of saturated hydrocarbons, tar acids and characteristic concentrations of heteroatomic hydrocarbons and biomarkers. High temperature signatures include enriched parent PAH. In addition, the organic petrographic features of the particulates or solid residuals can reveal additional source-specific information useful in the identification of fugitive tars and tar products. Environmental forensic laboratories capable of measuring these source signatures can often identify the tar origins and apportion the relative contribution of each origin based on the tar chemistry and physical properties.

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