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Isn’t it great when the kids play nice and get along? This spring, the EPA sat down with the state governments, the American Society for Testing and Materials, Amoco Oil Corp., British Petroleum Oil Co., Chevron USA, Exxon Co. USA, Mobil Oil Corp and Shell Oil Co., (perhaps you’ve heard of some of these folks…) and agreed to create a partnership to reduce the risk from leaking underground storage tanks by targeting those releases for cleanup which pose the greatest risk to public health and the environment.

This approach will ensure that high risk sites receive the greatest attention while still allowing cleanups to progress at all sites. As of the end of fiscal year 1995, states and EPA had confirmed more than 303,000 releases from underground tanks storing petroleum products. Cleanups have already been completed at over 131,000 sites. With 600 new releases discovered each week, however, state environmental programs face a growing cleanup workload. (So much for the doom-sayers who believe the cleanup market has peaked. Quit whirring, and pick up a broom for cryin’ out loud!)

Each of the partners contributed $100,000 toward development and delivery of a series of training session for interested states to teach the new risk-based approaches to cleanup. The industry partners are joined by Unocal, American Petroleum Institute, Petroleum Marketers Association, Environmental Bankers Association and Environmental and Commercial Insurance Inc. to provide technical expertise, resources, demonstration sites, peer review and other support. Sixteen of the 43 participating states have already completed the training to modify their cleanup programs and are moving toward incorporating risk-based approaches. The partnership will ensure that support is available to any state interested in designing a risk based approach to cleanups.

I think this is excellent. It has all the elements I like: cooperation, education and, of course, money.

Susan Parker

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Bugs beneath the runway

Bioaugmentation proves to be the best choice to clean up jet fuel beneath airport tarmac

By Jack Roberts and Andrew Mytinger

In-situ bioaugmentation and bioventing were combined to successfully treat a large Jet A fuel plume beneath the runway at Van Nuys Airport in southern California. The site is in the central portion of the San Fernando Valley, about 240 meters above sea level. The ground surface is flat and slopes toward the Los Angeles River, located approximately 5 kilometers to the south. The San Fernando Valley is an alluvial groundwater basin bounded by the San Gabriel and Santa Monica Mountains. The maximum depth of alluvium in the valley is 300 meters. The eastern part of the valley is underlain by coarse-grained sand and gravel deposits, while the western portion is underlain by fine-grained clay and silt. Sediments beneath the airport site consist of fine-grained sand and silt in interfingered layers and lenses to 40 meters below ground surface.

Pipeline and underground storage tank leaks released an estimated 133,000 liters of Jet A fuel into about 9800 cubic meters of soil beneath the tarmac. Total petroleum hydrocarbon (TPH) concentrations in the soil varied up to 24,000 ppm.

The responsible party, a tenant at the airport, chose a proposal from Biotreatment Inc., The Critter Co., (BTT) of San Diego, Calif., to clean up the site with a combination of in situ bioaugmentation and bioventing. BTT's proposal was 50 percent less expensive than other proposals, and had a projected schedule of 12 months, vs. three to five years for vapor extraction. The tenant also felt the plan would minimally disrupt ongoing airport operations. They rejected any plan that called for excavation due to the expense and disruption to airport activities.

The site is a deep water area with depth to groundwater exceeding 75 meters.

The fueling facility is located adjacent to a major runway in a secure area with restricted personnel access. Land use surrounding the site is strictly for aircraft storage, maintenance and flight operations. The tarmac extends at least 300 meters in all directions.

Groundwater was not affected, and the site was considered low risk. Target action levels were calculated from California's Leaking Underground Fuel Tank (LUFT) Manual Leaching Potential Analysis, and from California Regional Water Quality Control Board interim guidelines. Based on site conditions, 10,000 ppm of Jet A was determined to be acceptable action level. The remediation goal
bioaugmentation system technology products, featuring blends of naturally-occurring bacteria selected for their rapid reproduction and ability to consume a wide range of hydrocarbons at accelerated rates.

The first requirement for the bioinoculant formulation was to evaluate soil conditions. A representative soil sample was given to ProBioS for analysis. Indigenous microbial activity in the sample was recorded by a microscope with video capability. Nutrients, trace minerals, oxygen levels, pH and moisture were determined and analyzed. These data, along with site assessment analyticals on the contamination, were used to develop the microbial solution formulation, application rate and treatment protocol.

The bioinoculant consisted of products manufactured in Seattle, Wash., by Ultra Coatings Inc., incorporating microbes in a solution for matrix enhancement. Oil Breaker is a microbial solution product for petroleum hydrocarbon remediation that allows water and hydrocarbon molecules to merge. When this integration occurs, the surface area for microbial activity increases, and the hydrocarbon becomes immediately available as a food source for the bacteria. Oil Breaker enhances the percolation rate of the soil, adjusts matrix pH, buffers substances toxic to the bacteria and increases oil and water interfaces.

The Oil Breaker, UC-40 microbes, along with water soluble nutrients and oxygenated water were combined in calculated ratios and gravity fed into the matrix in multiple applications. The application method must take into account soil conditions, permeability changes, moisture content and natural barriers that might inhibit even distribution of the inoculate. The quantity of inoculant entering each zone was monitored to ensure uniform

was to reduce the levels below the target action levels and continue remediation until the degradation curve flattened out.

The site has four underground tanks: two 76,000 liter Jet A tanks, one 76,000 liter aviation gasoline (AVGAS) tank, and a 7600 liter waste oil tank. The 76,000 liter AVGAS tank is connected to a dispenser island by a fiberglass pipeline. The tanks were upgraded in 1995, and the hydrant supply lines removed.

In August of 1992, a site investigation discovered contamination in the soil beneath the tank farm. In 1993, additional investigations were performed to assess the cause of a product shortfall recorded at over 133,000 liters. Two areas contained elevated hydrocarbon concentrations—one area surrounding the hydrant pipeline leak, and another beneath the northwest corner of the fuel tanks. Highest detected hydrocarbon concentrations near the pipeline leak were 24,000 ppm. The main plume covered an area 36 by 13 meters, as deep as 27 meters. The second plume, under the tank farm area, was approximately 14 meters in diameter and extended to over 20 meters below grade.

BTI joined forces with another San Diego company, ProBioS, Inc., to provide microbial products and technical support for the bioaugmentation project. ProBioS is a distributor of UC-40™
distribution throughout the plume. A proprietary biocatalyst, supplied by BTI, provided oxygenated water for the degradation process. After 30 days, additional oxygen was provided through a bioventing system.

Progress throughout the project was monitored against baseline comparisons in three areas: by-products of metabolism, microbial activity and contamination concentrations.

Changes in carbon dioxide levels are good indicators of microbial activity. Increased CO\textsuperscript{2} occurs during periods of highest consumption. As degradation continues, CO\textsuperscript{2} production drops in relation to the diminishing number of hydrocarbons available. Carbon dioxide levels increased from a baseline of 2 percent to 6 percent after inoculation. After four months, the levels stabilized at 4 percent.

ProBioS used a microscope with custom optics and video capability to create a visual record of microbial activity. Before inoculation, a baseline record was created of the indigenous bacterial activity. It showed moderate activity, with no visual signs of degradation. After the initial solution applications, the augmented population was seen to be well established in the matrix. Compared to the baseline record, the augmented population appeared to be dense and highly active. Reproduction was occurring and there was visual evidence of degradation. ProBioS and BTI used this information to formulate treatment procedures to match changing conditions in the subsurface.

The TPH levels from the site assessment served as the baseline for contamination concentrations. Each month, soil samples were taken every 3 meters, at depths to 30 meters, using a CME 75 drill rig. Samples were sent to a state certified lab for analysis. The sampling was supervised by a registered geologist, and the analytical results of the EPA Method 8015 test were plotted. The mean TPH values in the soil were reduced by an average of 80 percent over a 90 day period, at which time monitoring showed that the degradation rate had leveled off at 2000 to 2500 ppm—75 percent below action levels. Even the highest TPH levels were 25 percent below action levels. It was apparent that as the degradation curve had leveled off, without additional inoculations, future remediation would be much slower. Options for continued mitigation were:

- Continue to maintain and monitor the existing biosystem. The bioremediation process depends on maintenance of a proper mixture of oxygen, nutrients, microorganisms and hydrocarbons. As the hydrocarbons in the soil diminish, it becomes more difficult to maintain the degradation components in proper mixture. Degradation continues with the existing bacteria metabolizing the hydrocarbons, but the process slows down. Continued maintenance would not significantly improve the conditions at that point.

- Reinoculate to try to reduce TPH levels even further, but the cost vs. benefit of reinoculation did not seem to be justified at this site.

- Close the site with no further action, which requires a determination that contamination levels pose a minimal risk to public health and the environment. Termination of remediation activity does not mean that bioremediation stops. Passive

bioremediation continues at the site.

Site closure depends on current or projected site use, attaining acceptable levels of contamination, and demonstrating low risk factors. It recognizes that 100 percent elimination of in situ contamination is unlikely, and uses target action levels based on land use, public contact and possible migration to drinking water. Closure of this site was based on target action levels from the LUFT Manual Leaching Potential Analysis and state Regional Water Quality Control Board interim guidelines for soil.

Based on the fact that the remediation effort has removed over 80 percent of the contamination, and that remaining levels are 75 to 80 percent below target action levels, the lead regulatory agency closed the site.

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Proper tools chew through debris

Firm takes dual approach to clean up lead

On-site treatment of hazardous waste is always a challenge when it's happening at an active facility. Space is often limited, time is usually limited, and money is always limited. Performing the remediation without interrupting the client's operation is a major concern. When an active battery manufacturing site in southeastern Pennsylvania found soils contaminated with lead levels exceeding 500 mg/l, they asked Advanced Remediation and Disposal Technologies Inc., (ARDT), Coopersburg, Pa., to stabilize 3000 cubic meters of lead-contaminated debris.

TCLP (Toxicity Characteristic Leaching Procedure) lead levels of the material, which consisted of contaminated concrete and refractory brick exceeded 500 mg/l. To save clients' money, ARDT methods use locally available reagents in their mix designs. They use cementious reagents in the form of cement and cement kiln dust, flyash, blends of sodium phosphates and magnesium oxides, depending on specific conditions such as contaminant type, level of...
contamination, the waste matrix and the ultimate disposition of the treated soil.

For example, traditional flyash or cement-based stabilization compounds generate volume increases of 15 to 20 percent. Although these reagents are inexpensive in comparison to some, the costs for disposition of the treated material are also taken into account. In some cases, more expensive reagents are better suited for a particular site because their volume increases can be as low as 4 percent.

“‘The popular thing to do has been to develop a proprietary reagent for treating the waste,’ says Shawn O’Donnell, president of ARDT. ‘But the chemistry is well known. The goal is to make the metals insoluble so they cannot leach. We decided not to market a proprietary reagent. Instead, we look for locally available reagents and evaluate what will be the most cost-effective solution.’

Historically, the most common method to treat hazardous material was to excavate and haul the waste to a RCRA (Resource Conservation and Recovery Act) landfill, with high disposal costs. But the most efficient and cost effective method is to treat the material on site and replace it in the ground.

At the battery manufacturing site, because the site was active, and the voids created by the excavated soil

Continues on page 12→
Proper tools, from page 11

were to be used for new construction, on-site reuse was not an option. Area Subtitle C landfill disposal costs are around $145 to $180 per metric ton, and Subtitle D costs are around $45 to $55, so ARDT decided that crushing and on-site treatment with off-site Subtitle D landfill disposal would be the most cost-effective method to treat the hazardous debris.

ARDT obtained approval from the Pennsylvania Department of Environmental Protection for the first phase of the project, which was the first approval awarded for on-site stabilization at an active facility within the state. And, since the stabilization method does not generate any off-gases, there are no regulatory issues involving air permits.

The first phase of the project involved 9000 metric tons of lead-contaminated soil and debris. While this phase was completed on time and on budget, ARDT used a 27 metric ton per hour pugmill and leased a crusher. The screen on the crusher was an older style, and allowed more clays and other materials through that slowed the operation. So, for the second phase, ARDT tried different equipment, which improved processing speed and efficiency. “But it wasn’t until we went in for the third phase that we hit peak performance,” says O'Donnell.

After the second phase, ARDT went to L.B. Smith Inc., a nearby equipment dealer. Through them, ARDT leased a model 52 pugmill with 300 barrel silo, a Kolberg stacker, a Pioneer 5260 closed circuit crushing plant and a model 1047 fine-jaw portable crusher, all manufactured by the construction equipment division of Portec, of Yankton, S.D.

Because the third phase of the job involved about 2700 metric tons of contaminated soil, and about 2700 metric tons of contaminated concrete and refractory brick, ARDT used the 5260 closed circuit crusher to bring the larger chunks of concrete down to about 35 to 40 millimeters. The portable fine-jaw crusher was used to crush the smaller debris, such as refractory brick to that same size.

“Volume increase was really not a major issue with this job, so we used a mixture of cement and cement kiln dust as our stabilizing reagent,” says O'Donnell. The Portec silo was filled with the reagent mixture and electronically connected to the pugmill. A scale on the conveyor allowed ARDT to electronically gauge the correct reagent mix for the weight of the material going into the pugmill. The mix design was the same as for the first two phases of the project.

In a hazardous cleanup situation, it is unusual to use a crusher as large as the 5260 closed circuit plant. In the case of the battery site, however, there was an unusually large quantity of large concrete to be crushed. A portable crusher, such as the fine-jaw model is more commonly used in environmental projects.

“It’s amazing how much difference the equipment can make,” says O’Donnell. “For example, the pugmill is the most expensive piece of equipment on the job because it dictates how long the job will take. At 180 metric tons per hour, the Portec pugmill was almost seven times faster than the pugmill we used originally, and it didn’t break down once. When a pugmill breaks down, you’re looking at a cost of about $1,500 a day in wages and supporting equipment costs.”

Write in 078

Write in 683
Try bio down under

Packed bed bioreactors enhance in situ bioremediation

by Dr. Ralph J. Portier and S. Reddy Chitta

The high cost of environmental remediation, and frequently, the liability associated with the use of conventional techniques such as landfiling, encourages the industry to search for innovative approaches for in place treatment. In situ bioremediation is gaining more acceptance and has proven to be cost effective. Research conducted in the 1980s and 1990s at the Institute of Environmental Studies, Louisiana State University (LSU), in Baton Rouge, to design immobilized packed bed reactors for biological treatment of contaminated groundwater and industrial process waters has fostered the idea of using the same technology for treatment of petroleum contaminated soils and groundwater, in-place. Aboveground, immobilized, packed-bed bioreactors have been used effectively to treat petroleum hydrocarbons, chlorinated solvents and pesticide contaminated water. Through the research conducted at LSU in the last decade, microbial strains have been developed for detoxification of specific compounds by using an aquatic microcosm system. Numerous microorganisms developed by LSU have been isolated from field samples of the sediment or sludge from highly contaminated sites.

Ralph Portier, Ph.D., is professor of environmental studies, Center for Coastal Energy and Environmental Research, Louisiana State University, Baton Rouge, La. S. Reddy Chitta is senior project manager, Envirosystems Inc., Lafayette, La.

The immobilized packed-bed reactor system, filled with a bio-support medium, contains adapted microbes which have the enzymatic capability to mineralize the organic compounds of interest. The purpose of the packed bed is to provide a large surface area for microbial colonization. The bio-support medium is usually a chemically inert and physically stable quartz based diatomaceous earth material, which has a good pore morphology and high surface area. Adsorption or covalent bonding to this medium is the primary mechanism for immobilization. Bacterial immobilization involves the entrapment of cells onto the matrix. Once bound, the cells are then readily accessible to the surrounding substrate.

The same bioreactor concept has been used by LSU and Envirosystems Inc., Lafayette, La., to design and develop immobilized packed-bed bioreactors (Bioplug and Bioconduits) for treatment of petroleum contaminated soils and groundwater, in-place. Bioplug are vertically placed bioreactors installed with conventional drilling equipment. Bioconduits are horizontally placed bioreactors installed with directional drilling equipment.

Generally, the adapted microbial strains used for immobilization in these bioreactors are selected from the indigenous microflora which have been identified to have the ability to degrade the contamination. Use of indigenous microflora reduces the time of microbial acclimation to the surrounding soil conditions and lowers the rejection rate. Once

Continues on page 14→
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Recycling of contaminated soil and industrial waste.

Bio down under, from page 13

placed in the subsurface, the Bioplugs and Bioconduits contain and sustain the high microbial populations required for effective degradation.

The cell loading optimum is determined with microbial adenosine triphosphate (ATP) approaches. Adapted bacterial counts and microbial ATP tests, which estimate immobilized biomass performance, conducted on the aliquot extracted from biosupport medium, indicate a stable microbial population of $10^{11}$ cfu/ml (colony forming units per milliliter) on the surface of the medium and $10^{9}$ cfu/ml within the inner core of the medium.

Bioplugs and Bioconduits are designed with ports for nutrient and air/oxygen amendment to maintain optimum conditions. Operational flow is maintained by initiating a pressure gradient in the reactors with an oxygen source. The air flow rate design is based on site specific conditions and the contaminants—volatile organic compounds or semi-volatile organic compounds—to be remediated. Use of contaminated groundwater or site water through the immobilized bed results in mineralization of organics and generation of excess biomass in the form of whole cell bleed-off from the bed. The elevated biomass is allowed to escape from the Bioplugs and Bioconduits, thus
introducing an enriched, adapted microflora into the surrounding soil strata in a radial fashion.

This technology has been successfully implemented by LSU and Envirosystems Inc. in remediation of organic compounds at several leaking underground storage tank and industrial sites.

Case Study 1
A truck stop facility with diesel contamination in an area of about 5,000 square meters had initial TPH-diesel concentrations to approximately 10,000 ppm, extending to a depth of 3 meters below ground surface. The soil was predominantly silty clay. Initial concentrations, as reported in the site assessment, are shown in figure one, page 14. An in situ immobilized bioremediation (Bioconduit) system was installed with directional drilling equipment. Approximately 2150 meters of Bioconduit, or bioreactor, filled with porous media to which the specific microbial degrader had been cultivated, were installed underneath the concrete slab with minimal disturbance to ongoing operations of the facility. Site conditions and remediation parameters were monitored to maintain optimum conditions for biodegradation. Monitoring samples were collected from the remediation area using a combination of stratified sampling and unaligned random grid sampling methods.

Continues on page 16→
Within 200 days of activation of the system, TPH diesel concentrations within the remediation area and the plume were reduced as shown on the map in figure two, page 15. Later, after reaching regulatory established clean-up levels, confirmation samples were collected at ten locations selected by the regulatory agency. Three discrete soil samples were collected from each sample location at depths of 1, 2 and 3 meters, and analyzed for TPH-diesel using the modified California DHS method. The concentrations of TPH-diesel at the site were within the regulatory acceptable levels, with one exception in a limited area recontaminated due to chronic leakage from the piping.

Approximately 152 cubic meters of recontaminated soil from this limited area has been disposed at a permitted off-site facility. The regulatory authorities approved a request for no further action and site closure.

Case Study 2
A gasoline station with gasoline and waste oil contamination in an area of approximately 1620 square meters extending to a depth of 3.5 meters below ground surface has been remediated to the regulatory acceptable standards using this in situ bioremediation technology. The soil lithology in the zone of contamination primarily consisted of clayey silts and silty clays. The initial site assessment revealed gasoline concentration (as identified by the modified California DHS method) ranging from below detection limits to 2100 ppm and waste oil (Oil & Grease) concentrations (as identified by EPA method 5520 E&F) from below detection limits to 6500 ppm. The contamination plume as developed from the site assessment is shown in figure three, above. Additional sampling conducted during the remediation period indicated elevated levels (22,000 ppm) of Oil & Grease within the remediation area. After conducting an unsuccessful pilot scale study of a vacuum extraction system, the Bioconduit approach was implemented. Approximately 820 meters of Bioconduit was installed underneath the concrete slab and existing structures with minimal disturbance. The reactor contained bio-support media to which the adapted microbial degrader was immobilized.

Samples collected using a combination of stratified sampling method and an unaligned random grid sampling method indicated that while gasoline concentrations were reduced significantly in a relatively short period of time,
Oil & Grease contamination required more time for remediation. However, within a year of activation of the remediation system, the concentration of Oil & Grease was reduced to the regulatory acceptable levels. The reduction of Oil & Grease concentrations during the remediation period is shown in figure four, right. A request for no further action and site closure has been approved by the regulatory authorities at this site as well.

Case Study 3
Over the last 30 years, leakage and accidental discharge of petroleum-based lubricating oil used to maintain the pipeline and related equipment of a gas transmission facility have resulted in petroleum hydrocarbon contamination of the soil. The site evaluation conducted by a private engineering firm identified 50 areas at four different sites exhibiting hydrocarbon concentrations greater than regulatory acceptable levels. Fifteen of the 50 areas were remediated by installing approximately 550 in situ immobilized bioreactors (Bioplug). A monitoring protocol developed for the site was implemented during the remediation period to maintain optimal conditions and make operational adjustments, as required.

The Bioplug system was designed to place hydrocarbon

Continues on page 18→

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Bio down under, from page 17

degrading microorganisms in close contact with the contaminants. Initial total petroleum hydrocarbon concentrations as analyzed by EPA method 418.1 at one of the 15 target areas were as high as 16,000 ppm with an average concentration of 4,400 ppm. Samples were collected at different radial distances and depths from each Bioplug location within the subject area. The samples were analyzed to determine the effective radius of influence for each Bioplug. Analysis of covariance indicated that TPH degradation occurred at an equivalent rate at all depths and distances sampled and analyzed during the degradation period.

Changes in polynuclear aromatic hydrocarbon (PAH) composition were monitored by gas chromatography/mass spectrometry. Samples were analyzed for PAH content and concentration. Fourteen PAH compounds were identified in varying concentrations during the day 14 sampling. By day 90, PAHs with three or fewer rings were completely degraded. However, low concentrations of

flouranthenes, benzo(a)pyrene, benzo(b) fluoranthene, and indeno(123cd) pyrene were identified after 90 days of remediation. The presence of 4+ ring PAHs was expected as the ability of microbes to mineralize PAHs decreases with increasing ring number.

These assays were coupled with microbial measurements of total heterotrophic and total petroleum degrading bacteria, and direct measurements with acridine orange fluorescent staining. Changes in the population of petroleum hydrocarbon degrading microorganisms over time in the subject area were determined by averaging the values obtained from all samples collected within the area. The microbial growth and the degradation of the contamination occurred exponentially within the first thirty days. Microbial growth was observed to decrease after thirty days when the majority of the easily degraded petroleum hydrocarbons, saturated alkanes, and PAHs containing fewer than three rings had been depleted by approximately by 72 percent. Sampling and analysis during the remediation period indicated an increase in the heterotrophic and
petroleum degrading microbial population by 75 percent and 57 percent, respectively, from day 14 to day 90. Within 180 days from the activation of the remediation system, targeted compliance TPH concentrations of 100 ppm were attained. The reduction of TPH concentrations over time is shown in figure five, right.

These bioreactor systems can be designed by incorporating vadose zone and groundwater modeling. Based on the availability of site hydrogeologic data and conditions, analytical modeling and/or numerical modeling can be used to design in situ bioremediation of the saturated zone.

A bioreactor system can offer an advantage over enhanced bioremediation by reducing the time of remediation. Also, the frequently encountered problem of ineffective indigenous microorganisms and/or low indigenous microbial population can be avoided. Bioreactors increase the petroleum degrader population by placement of the adapted microorganisms in close contact with the organic residue. The in situ immobilized bioreactors can also be used to provide a co-metabolite for degradation of hazardous by-products produced during the degradation process of some of the chlorinated solvents.

An in situ immobilized bioreactor system can be used in conjunction with a vapor extraction system. In many cases, the mass removal efficiency of VOCs in vapor extraction systems declines over time and depends on numerous factors. The use of in situ bioremediation in conjunction with a vapor extraction system combines mass reduction and mass transfer phenomena, thus reducing the time of remediation and the cost of cleanup. Use of these systems in tandem also enables one to monitor the oxygen uptake by the microorganisms for the degradation process.

Depending on site conditions, an in situ immobilized bioreactor system can also be used with a pump and treat system. The pump and treat method can change the hydraulic gradient for effective nutrient movement within the subsurface and provide sufficient contact time for dissolved oxygen and nutrients, thus promoting effective degradation.

In many cases, due to the complex nature of subsurface conditions, a combination of in situ remediation techniques is recommended. With rigorous engineering design, in situ technologies such as vapor extraction, air sparging, bioventing and biopulsing can either be modified and/or used with in situ immobilized bioreactor technology.
A look at degradation of CAHs

Chlorinated aliphatic hydrocarbons degrade by reductive dehalogenation and co-metabolism

By Richard Schaffner, Jr., P.G., Edward Hawkins, C.G., and James Wieck

Bioremediation screening study results indicate that chlorinated aliphatic hydrocarbons (CAHs) are undergoing intrinsic bioremediation at a former municipal wastewater treatment facility in southern New Hampshire. Certain CAHs may be transformed to carbon dioxide, water, chloride and/or intermediate products by co-metabolism and reductive dehalogenation. Although a variety of attenuation mechanisms control the fate of CAHs in groundwater systems, two important mechanisms are co-metabolism and reductive dehalogenation. Co-metabolism involves microbial utilization of a primary substrate, or organic carbon and energy source, and serendipitous concomitant destruction of CAHs with no added benefit to the microbes. Reductive dehalogenation involves transfer of electrons by microbes to CAHs and their subsequent transformation to daughter species. In general, co-metabolism and reductive dehalogenation are important CAH-attenuation mechanisms under oxic and anoxic conditions, respectively.

Certain CAHs, such as trichloroethene, (TCE, ClHC=CCl3), 1,2-dichloroethenes (1,2 DCEs) and vinyl chloride (VC) may be transformed co-metabolically. Co-metabolism may be induced by certain methylo trophic bacteria that use CH4 or methanol (CH3OH) as substrate and oxygen (O2) as electron acceptor. Methanotrophs, a subgroup of the methylo trophs, are obligate aerobes that produce enzymes, principally soluble methane monoxygenase, (sMMO) which catalyze both CH4 and CAH transformation. Equation one illustrates CH4 oxidation, equation two illustrates TCE oxidation:

\[
\begin{align*}
\text{CH}_4 + 2\text{O}_2 & \xrightarrow{s\text{MMO}} \text{CO}_2 + 2\text{H}_2\text{O} \quad (\text{equation 1}) \\
2\text{Cl}1\text{HC} & = \text{CCl}_2 + 4.5\text{O}_2 \xrightarrow{s\text{MMO}} 4\text{CO}_2 + \text{H}_2\text{O} + 6\text{Cl} \\
\end{align*}
\]

(equation two)

---

**Figure one**

Richard Schaffner, Jr., P.G., is a technical specialist; Edward Hawkins, C.G., is a senior project manager; and James Wieck is an assistant project manager for GZA GeoEnvironmental Inc., Manchester, N.H.
Note that reaction mechanisms involve intermediate steps and products not considered in these equations. CH₃OH and TCE epoxide are intermediates of equations one and two, respectively. Nevertheless, these equations illustrate the overall process of ultimate CH₄ and TCE transformation under oxic conditions. Optimal conditions for CAH co-metabolism include a viable methylotroph population density which expresses sMMO, oxic conditions, and dissolved CH₄ at suitable concentrations. Low CH₄ concentrations may not stimulate sMMO expression, and high concentrations may out-compete CAHs for sMMO. In general, CAH co-metabolism potential increases with decreased number of halogens.

More halogenated CAHs typically do not easily break down co-metabolically, but are susceptible to reductive dehalogenation under anoxic conditions. For example, tetrachloroethene (PCE) can liberate Cl⁻ to form TCE provided a free electron is available for the exchange. TCE can be further transformed to 1,2-DCEs and VC by reductive dehalogenation. Reductive dehalogenation may be induced by anaerobic bacteria that use hydrogen (H₂) or certain organic compounds such as CH₃OH as electron donors, and then transfer the electrons to CAHs inducing dechlorination to daughter species. The following chemical equations depict oxidation of CH₃OH and dechlorination of PCE (Cl₂C = CCl₂) to ethene (H₂C = CH₂), hydrochloric acid (HCl) and CO₂ (equation three), and the oxidation of H₂ and dechlorination of PCE to TCE and HCl (equation four).

1.33CH₃OH + Cl₂C = CCl₂ + 1.33 H₂O -> H₂C = CH₂ + 4HCl + 1.33 CO₂ (equation three)
Cl₂C = CCl₂ + H₂ -> CH₂C = CCl₂ + HCl (equation four).

Equations three and four consider only one electron donor—CH₃OH in equation three, and H₂ in equation four—but illustrate the overall process of PCE transformation under anoxic conditions. Other intrinsic dechlorination processes occur, including transformations accommodated by chemically-reduced metals which serve as electron donors. However, equations three and four represent predominant attenuation mechanisms for many CAHs due to a link with microbial respiration.

Optimal conditions for reductive dehalogenation include a viable population density of anaerobic bacteria, anoxic conditions lacking electron acceptors other than CAHs, and suitable substrate concentration. In general, reductive dehalogenation potential increases with increased number of halogens.

The bioremediation screening study was performed to evaluate whether intrinsic bioremediation may be an important factor in CAH attenuation at a site located in southern New Hampshire. The 10.4 hectare site is occupied by a former municipal wastewater storage tank.

Continues on page 22
HYDROGEOLOGIC UNIT

<table>
<thead>
<tr>
<th>Monitoring Wells</th>
<th>Upper Overburden</th>
<th>Lower Overburden</th>
<th>Bedrock</th>
</tr>
</thead>
<tbody>
<tr>
<td>GZ-1A</td>
<td>GZ-2</td>
<td>GZ-3A</td>
<td></td>
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<tr>
<td>GZ-1L</td>
<td>GZ-8L</td>
<td>GZ-2L</td>
<td>GZ-1B</td>
</tr>
<tr>
<td>GZ-3L</td>
<td>GZ-4L</td>
<td>GZ-3B</td>
<td></td>
</tr>
</tbody>
</table>

X indicates information applicable to indicated hydrogeologic system.

**Figure two**

Treatment facility built in 1964, and closed in 1986. Facility structures are located on the northern portion of the site, while the southern portion is undeveloped. A small river abuts the site to the west, as shown in figure one, page 20.

Site stratigraphy generally consists of about 12 to 23 meters of overburden comprised of fill and up to four natural soil horizons. Fill is localized in areal extent, and contains up to 2 meters of septic sludge and reworked soil. Uppermost natural soil includes about 1.5 to 3 meters of fine sand and silt, underlain discontinuously by up to about 6 meters of clayey silt. The fine sand and silt (or clayey silt, if present) is underlain by up to about 1 to 3 meters of fine to coarse sandy glacial till that overlies about 3 to 9 meters of silty glacial till. Metamorphic bedrock consisting of moderately fractured and slightly weathered granofels and schist underlies overburden materials.

Saturated overburden groundwater at the site occurs in up to two hydrogeologic units designated as the upper and lower units, depending on the presence of the clayey silt horizon (aquitard). The upper unit occurs within the fine sand and silt horizon. Hydraulic conductivity (K) estimates for the upper unit are between about $10^{-2}$ to $10^{-4}$ centimeters per second (cm/s). The lower unit occurs within the upper sandy till and lower silty till horizons. K values for upper till are between about $10^{-3}$ to $10^{-4}$ cm/s, whereas K values for the lower till are about $10^{-4}$ to $10^{-6}$ cm/s. Where present, the clayey silt aquitard may partially confine the lower overburden unit.

Depth to overburden groundwater is about 3 meters, with seasonal variation of about 1.5 meters based on quarterly water level monitoring over the last several years. Groundwater level data from on-site multi-level monitoring wells indicate groundwater recharge conditions and a horizontal hydraulic gradient of about 0.003 for the upper hydrogeologic unit, and about 0.0006 for the lower unit. Groundwater flow direction within saturated overburden is westward toward the river. Bedrock groundwater flow occurs principally within fracture sets. The direction of flow within this unit is inconclusive.

During operations at the treatment facility, septic sludges containing industrial waste were periodically disposed in a pit located on the undeveloped, southern portion of the site. Dumping of septage is believed to
have occurred in this area as well. CAHs were first detected in site soils and groundwater in 1986 during trenching operations to construct a sewer main. In 1987, groundwater monitoring detected certain CAHs in samples of overburden and bedrock groundwater at concentrations up to 39 pg/l, 1,1-dichloroethene (1,1-DCE, 79 pg/l), 1,1-dichloroethylene (1,1-DCA), 7,211 pg/l, 1,2-DCEs, 1,200 pg/l, 1,1,1-trichloroethane (1,1,1-TCA), 58,000 pg/l TCE and 980 pg/l PCE. Ongoing groundwater monitoring indicates the presence of CAHs at concentrations in the 10^3 to 10^4 pg/l range. Concentrations of parent CAH in the form of TCE, and intermediate CAHs, 1,2-DCEs, have decreased over time in groundwater samples collected from overburden monitoring well GZ-4L, whereas daughter CAH, as VC, concentrations have increased in groundwater samples collected from overburden monitoring wells GZ-2, GZ-3L and GZ-4L. Parent CAHs are assumed to be chemical reactants and daughter CAHs are assumed to be products of these reactants.

Based on subsurface conditions at the site, a feasibility study was performed to select a groundwater treatment technology. The study included a bioremediation screening study to evaluate whether intrinsic bioremediation may be an important CAH attenuation mechanism at the site. Unique characteristics of historic waste disposal practices provided impetus for the study. Though it was recognized that reductive dehalogenation may be an important attenuation mechanism, the study focused on co-metabolism potential because this process may be enhanced to degrade the CAH suite detected at the site, notably VC. VC is a common daughter product of reductive dehalogenation, and has the lowest EPA MCL of the CAH suite at 2 pg/l. The study

Continues on page 24

<table>
<thead>
<tr>
<th>HYDROGEOLOGIC UNIT</th>
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<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>Upper Overburden</td>
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<tr>
<td>Bedrock</td>
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<td>GZ-3L GZ-4L GZ-1B</td>
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<tr>
<td>GZ-3B</td>
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<tr>
<td>5.2 5.0 3.7</td>
</tr>
<tr>
<td>0.7 5.4 4.2</td>
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<tr>
<td>3.9</td>
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<tr>
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<td>+85</td>
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<td>Specific Conductance (umhos/cm)</td>
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<td>594 623 366</td>
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<td>Temperature (°C)</td>
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<tr>
<td>12.7 11.5 12.7</td>
</tr>
<tr>
<td>10.7</td>
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</tbody>
</table>

1. Boldface print indicates background sampling location and datum.
2. mg/l indicates milligrams per liter; mV indicates millivolts; umhos/cm indicates micromhos per centimeter; and °C indicates degrees Centigrade.

Figure three

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### HYDROGEOLOGIC UNIT

<table>
<thead>
<tr>
<th>Monitoring Wells</th>
<th>Upper Overburden</th>
<th>Lower Overburden</th>
<th>Bedrock</th>
</tr>
</thead>
<tbody>
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<td>CH₄ µg/L</td>
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<td>&lt;10</td>
<td>&lt;10</td>
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<td>1,1,1-TCA</td>
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<td>TCE</td>
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<td>&lt;1 &lt;1 380 ≤250 800 ND 83</td>
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<td>1,1-DCE</td>
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<td>TOTAL CAHs</td>
<td>ND ≥200 7</td>
<td>ND ND 41060 25460 7725 ND 2403</td>
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1. ND indicates that though the sample was not analyzed for respective parameter during the sampling round, it had not previously been detected at this location above the method detection limit (MDL); NA indicates not analyzed for respective parameter; < indicates detected below MDL shown.

2. Total CAHs refers to total CAH concentration. For CAHs not detected above MDLs, a value of one half the MDL was used to calculate total CAHs. For CAHs detected below the MDL, a value equal to the MDL was used to calculate total CAHs. Total CAH concentrations were rounded to the nearest whole number.

3. Boldface print indicates background sampling and datum.

---

**Figure four**

- Field screening groundwater samples for the water quality indicator parameters of dissolved oxygen, oxidation-reduction potential, pH, specific conductance and temperature to evaluate groundwater quality conditions.
- Analysis of groundwater samples for certain CAHs and CH₄ to evaluate contaminant and primary substrate concentrations to evaluate co-metabolism potential, and comparison of current analytical data with historical data; and
- Enumeration of groundwater samples for methyloptrophs to evaluate population density magnitude and distribution.

Groundwater samples were collected from monitoring wells in each hydrogeologic unit at both contaminant plume and background locations, as summarized in figure two, page 22. Data from background locations serve as controls for biochemical processes occurring within the contaminant plume. Groundwater samples were collected with bailers from three upper overburden, five lower overburden and two bedrock monitoring wells. More than three well volumes of groundwater were removed from monitoring wells prior to sampling. Bailers were used to purge upper overburden wells, inertia pumps for lower overburden wells, and electrical submersible pumps for the bedrock wells.

Samples for field screening were analyzed at the time of collection for dissolved oxygen, pH, temperature, and specific conductance with an Industrial Chemical Measurement Water Analyzer Model 51600 and for...
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<thead>
<tr>
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<th>Bedrock</th>
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<td>Wells</td>
<td>GZ-1A</td>
<td>GZ-2</td>
<td>GZ-3A</td>
</tr>
<tr>
<td>Methylotrophs cfu/ml</td>
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<td>10^4</td>
</tr>
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</table>

1. SD indicates samples destroyed; no data entry indicates sample not collected for microbial enumeration.
2. Boldface print indicates background sampling location and datum.
3. * indicates that microbial activity was similar for both test and control vials; however, relatively high ambient CH₄ concentrations in these samples (i.e., 810 µg/l, GZ-2L: 1900 µg/l, GZ-3L) likely supplied primary substrate to indigenous methylotrophs.

Figure five

oxidation-reduction potential with an Oakton™ ORPTest™ model 35650-00. Field screening results are summarized in figure three, page 23.

Concentrations of dissolved oxygen range from 0.7 to 5.8 milligrams per liter (mg/l). Contaminant plume locations generally have depressed dissolved concentrations relative to background within both overburden and bedrock groundwater, for example, 0.7 mg/l at well GZ-3L. Values for oxidation-reduction potential range from -45 to +210 mV. In general, oxidation-reduction potential values for each hydrogeologic unit within the contaminant plume also are depressed relative to background, for example, -45mV, monitoring well GZ-3L. The pH, specific

<table>
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<td>29</td>
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<tr>
<td>Daughter CAHs</td>
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<tr>
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November 1993

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<td>Daughter CAHs</td>
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November 1994

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<tr>
<td>Total</td>
<td>16285</td>
<td>100</td>
<td>700</td>
</tr>
</tbody>
</table>

December 1995

1. ND indicates not detected above MDL. For CAHs not detected above MDLs, a value of one half the MDL was used to calculate total parent/daughter CAHs. For CAHs detected below MDLs, a value equal to the MDL was used to calculate total parent/daughter CAHs. Concentrations were rounded to the nearest whole number. Note that analyses were performed by different analytical laboratories and EPA methods.
2. % indicates percent of total CAH concentration for respective sampling round. -- indicates monitoring well was not installed.

Figure six

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conductivity and temperature data range from 5.2 to 9.1 standard units, 147 to 623 micromhos per centimeter, and 10.1 to 12.7° C respectively, and are similar for both contaminant plume and background locations.

Groundwater samples were collected by EPA protocol and submitted to an analytical lab for CAH and CH<sub>4</sub> analyses. Analyses for CAHs were performed in accordance with EPA Method 8010. Analyses for CH<sub>4</sub> were performed with static headspace / gas chromatographic methods. Lab results are summarized in figure four, page 24.

Laboratory testing detected total CAHs at concentrations ranging from 7 to 41,060 µg/l within groundwater samples collected from contaminant plume locations. The contaminant signature consisted of parent CAHs 1,1,1-TCA and TCE, and associated daughter CAHs 1,1-DCE, 1,1-DCA, 1,2-DCEs and VC.

Dissolved phase CH<sub>4</sub> was detected at concentrations up to 1,900 µg/l. CH<sub>4</sub> was not detected above method detection limits in groundwater samples collected from either upper overburden or background lower overburden locations, but was detected at concentrations on the order of 10<sup>-5</sup> to 10<sup>-2</sup> µg/l in samples collected from lower overburden locations within the contaminant plume. The sample of bedrock groundwater collected from within the contaminant plume contained CH<sub>4</sub> at a higher concentration—470 µg/l from well GZ-3B—than the sample collected from the background location—200 µg/l from well GZ-1B.

Samples for methylo troph enumeration were collected in pre-sterilized containers, and enumerated at Custom Biologicals Inc., of Boca Raton, Fla. One 16 milliliter capacity test and one control vial were prepared per sample. A 9 ml solution of sterilized Bushnell-Haas broth was added to each vial. This inorganic nutrient supplement consists of magnesium sulfate, calcium chloride, monopotassium phosphate, dipotassium phosphate, ammonium nitrate and ferric chloride. A 1 percent solution by volume of CH<sub>3</sub>OH solution was added to each vial to stimulate methylo trophs, if present. CH<sub>3</sub>OH was selected as the primary substrate due to its higher aqueous solubility, relative to CH<sub>4</sub>, which makes it better suited for lab procedures. Moreover, certain methylo trophs can use CH<sub>3</sub>OH as a primary substrate, and can co-metabolize CAHs. A 1 ml aliquot of groundwater was added to each vial which was agitated to homogenize the sample. A series of aqueous solutions representing ten-fold dilutions of the sample was prepared from each test and control vial. Control vials containing Bushnell-Haas broth without CH<sub>3</sub>OH served as controls for other heterotrophs, which may be stimulated by broth amendment. Each dilution was incubated for 14 days at about 20° C, and population densities were estimated based on the observed distribution of positive and negative results in test vials relative to controls in accordance with standard Most Probable Number (MPN) statistical tables.

Methylo troph enumeration results are summarized in figure five, page 26. Population densities range from 10<sup>4</sup> to 10<sup>4</sup> colony forming units per liter (cfu/l). Methylo trophs were detected in groundwater samples collected from wells located within the contaminant plume, but not from those in background locations. Reductions in dissolved oxygen concentration at contaminant plume locations relative to background were generally observed within the upper

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overburden at 22 percent, in the lower overburden at 36 percent and 7 percent in bedrock hydrogeologic units. These data generally indicate oxygen-depressed conditions at contaminant plume locations for each hydrogeologic unit, most notably in the lower overburden. In general, reductions in oxidation-reduction potential values for contaminant plume locations relative to background also were observed for the upper overburden at 43 percent reduction, for the lower overburden at 60 percent reduction and for bedrock at 43 percent. Oxygen-reduction potential data indicate chemically-reducing conditions generally exist within the contaminant plume, particularly the lower overburden. Consistent with these data, there is a positive correlation between dissolved oxygen and oxidation-reduction potential. Low oxidation-reduction potential values and depressed dissolved oxygen concentrations, especially for the lower overburden, indicate oxygen depressed, chemically-reducing groundwater conditions within the contaminant plume relative to background. Dissolved oxygen and oxidation-reduction potential data for the sample collected from well GZ-4L (lower unit) reflect oxic, chemically-oxidizing conditions likely because this location is sidegradient of the sludge and septage disposal pit. Though these data do not indicate entirely anoxic, chemically-reducing conditions, sampling with bailers can artificially increase dissolved oxygen concentrations. Therefore, dissolved oxygen and oxidation-reduction potential values are conservative and may be lower in situ.

Because the contaminant signature consists primarily of CAHs that are not substrates for indigenous heterotrophs, depressed dissolved oxygen concentrations and oxidation-reduction potential values within the contaminant plume are not caused by CAH metabolism. Rather, these data are indicators of groundwater conditions caused by historic disposal of sludge and septage that likely contained significant organic carbon, inorganic nutrient and biomass. Sludge and septage likely exert strong biochemical oxygen demand, thereby depleting ambient dissolved oxygen and shifting oxidation-reduction potential toward chemically-reducing conditions. The EPA estimates untreated septage can exert a seven day biochemical oxygen demand of up to 3,195 milligrams of oxygen per liter, and a

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chemical oxygen demand of up to 7,998 mg of oxygen per liter. In 1989, D.L. Freedman and J.M. Gossett demonstrated that reductive dehalogenation driven by methanogenic activity dechlorinated PCE and TCE to VC in the presence of wastewater-digested sludge—as reported in volume 55 of Applied Environmental Microbiology.

In general, current groundwater conditions within the contaminant plume likely limit methylotrophic activity, as these microbes require oxic conditions to be viable. However, site conditions may support methanogenic activity. Though data reflect oxygen depressed, chemically-reducing groundwater conditions at the time of sampling, these conditions may vary both temporally and spatially within the plume. Variations in the location of oxygen loading may occur as a result of variability in:

- hydraulic gradients caused by precipitation and surface water / groundwater interactions; and
- subsurface distribution of sludge and septage.

Groundwater conditions conducive for methylotrophic—co-metabolic—activity, and methanogenic—reductive dehalogenation—activity are likely dynamic, though anaerobic conditions likely prevail at depth.

The pH, specific conductance and temperature data are consistent with data for other overburden and bedrock groundwater systems in southern New Hampshire, and are considered generally conducive for microbial activity.

Concentrations of total parent CAHs, total daughter CAHs, and ratios of total parent and total daughter CAH concentrations for three sampling rounds are summarized in figure six, page 26. In general, there is a trend of increasing percentages of daughter CAHs over time at most sampling locations. This trend is consistent with CAH degradation under anoxic, chemically-reducing conditions. Increased daughter concentrations indicate that attenuation due to reductive dehalogenation generally is more important than attenuation due to CH₄ co-metabolism. Specifically, increasing VC concentrations over time in samples collected from wells GZ-2 and GZ-3L indicate CH₄ co-metabolism is not as important as reductive dehalogenation at these locations, because VC may be destroyed co-metabolically given sufficient dissolved oxygen and CH₄ concentrations, and a viable methylotroph

Continues on page 30 →
CAHs, from page 29

population density. Elevated CH₄ concentrations at contaminant plume locations relative to background likely are related to historic sludge and septic disposal. Elevated CH₄ concentrations reflect active methanogenic activity driven by abundant substrate. Methanogens use sludge and septic as substrate and CO₂ as electron acceptor, and evolve CH₄ during metabolism. In general, the highest CH₄ concentrations were detected in groundwater samples collected from the lower overburden unit, which is consistent with dissolved oxygen and oxidation-reduction potential data for this unit. CH₄ was not detected in groundwater samples collected from the upper hydrogeologic unit, which may be related to water table proximity. For example, oxygen-saturated recharge from precipitation and passive air diffusion through unsaturated zone soils may supply sufficient oxygen to inhibit methanogenesis, and/or may stimulate CH₄ uptake by indigenous methylotrophs. In addition, CH₄ may be volatilizing into the unsaturated zone from groundwater.

Ambient CH₄ in contaminant plume groundwater may stimulate CAH co-metabolism. However, CH₄ concentrations are about one order of magnitude less than total CAH concentrations for each hydrogeologic unit, suggesting that CAH co-metabolism may be limited as well as oxygen limited.

Data indicate the presence of viable methylotroph population densities in samples collected from wells GZ-3A in the upper unit, GZ-4L in the lower unit and GZ-3B in the bedrock unit, within the contaminant plume. Relatively low population densities, likely due to CAH toxicity, occur in the vicinity of wells GZ-2L and GZ-3L in the lower overburden unit. For example, total CAHs detected in groundwater samples from monitoring wells GZ-2L and GZ-3L were 41,060 and 24,460 μg/l, respectively. Complete microbial inhibition has been reported in the range of 50,000 to 150,000 μg/l TCE. Methylotrophs also may be oxygen limited, especially in the lower unit in the vicinity of well GZ-3L—0.7 mg/l dissolved oxygen. In addition, population density data for samples collected from wells GZ-2L and GZ-3L were similar for both test and controls. However, ambient CH₄ concentrations for samples collected from these monitoring wells were on the order of 10⁶ to 10⁷ μg/l, suggesting that methylotrophs were stimulated by ambient CH₄.

Methylotrophs were not detected in the sample collected from well GZ-2 in the upper unit. This

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condition likely reflects substrate limitation—<10 µg/l CH₄. The relatively high population density in the groundwater sample from well GZ-3A in the upper unit suggests that methylotrophs may be using a substrate other than CH₄—<10 µg/l CH₄—not present at the location of well GZ-2. Methylotrophs may be present at the well GZ-3A location, and not the GZ-2 location, because the former well is closer to the sludge pit that may be a source of alternative substrates.

Methylotrophs were not detected in groundwater samples collected from background well locations in either the lower overburden or bedrock hydrogeologic units, but were detected in samples collected from contaminant plume locations in these units at population densities up to 10⁶ cfu/l. The general distribution of methylotrophs—greater population densities in contaminant plume locations relative to background—suggests stimulation by dissolved-phase CH₄ within the contaminant plume, except where otherwise inhibited by CAH toxicity or low dissolved oxygen concentration. For example, groundwater samples collected from monitoring wells GZ-3A in the upper unit, and GZ-4L in the lower unit, generally had higher methylotroph population densities, higher dissolved oxygen concentrations, and higher oxidation-reduction potential values than samples collected from wells in other plume locations. These data are consistent with suitable conditions for CH₄ co-metabolism and lower daughter CAH ratios observed at these locations.

So, two CAH-attenuation mechanisms are indeed active at the site. Reductive dehalogenation is likely the principal attenuation mechanism. Co-metabolism may be operative to a lesser extent. Reductive dehalogenation occurs within anoxic, chemically-reducing portions of the contaminant plume where methanogenic conditions exist. Co-metabolism, driven by available CH₂O or other substrate, occurs within oxic, chemically-oxidizing portions of the plume, notably in areas with limited methanogenic activity. Both processes are driven by the historic disposal of sludge and septage with CAHs. Sludge and septage exerts biochemical oxygen demand which supports methanogenic conditions required for reductive dehalogenation. CH₄ evolved during methanogenic activity drives CAH co-metabolism. Though conditions suitable for methanogenic and methylotrophic activity may vary spatially and temporally at the site, reductive dehalogenation is likely more important than co-metabolism because:

- CH₄ concentrations are about one order of magnitude less than total CAH concentrations, and therefore may not induce sufficient sMMO expression to stimulate significant CAH co-metabolism in situ; and
- Significant increases in VC concentration over time at certain well locations suggests active reductive dehalogenation, given that VC can be readily destroyed by CH₄ co-metabolism.

CAH co-metabolism is oxygen and CH₄ limited at the site. Significantly, engineered controls involving pulsed oxygen and CH₄ amendment could be used to shift groundwater chemistry toward oxic, chemically-oxidizing conditions, and provide substrate, thereby stimulating co-metabolism in situ. Lab-scale treatability testing is underway to evaluate biostimulation strategies to enhance bioremediation.
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Biomounds pass tests in Minnesota

Field evaluation proves biomounds clean soils economically

By Brian Kamnikar, P.E.

The Minnesota Department of Transportation has developed a low technology composting treatment alternative. They have been recycling petroleum contaminated soil, animal manure and low grade wood chips in an environmentally sound process since 1991. Mn/DOT has successfully treated several thousand cubic meters of excavated petroleum contaminated soils by using the biomound treatment technique. The process has not only been effective but also has the advantage of being generally accepted by local bodies of government and the public with little opposition. Because the process is low maintenance, the biomound technique has shown substantial cost savings over alternative treatments.

Mn/DOT has removed hundreds of fuel underground storage tanks from their various maintenance facilities, and during highway construction projects since 1988. The majority of these tank removals have encountered petroleum contaminated soil as a result of leaking tank systems or spills experienced during product delivery.

The Minnesota Pollution Control Agency (MPCA) requires treatment of excavated petroleum contaminated soil to a current cleanup threshold for soils treated by landspreading or biomound technology of 10 ppm as total petroleum hydrocarbons. During the late 1980s, Mn/DOT primarily treated the contaminated soil by land application. Minnesota regulations generally allow only a single application of petroleum contaminated soils at an approved landspread location. Therefore, as appropriate landspread locations were used up and as the process became increasingly unpopular with the public, Mn/DOT was faced with the possibility of stockpiling thousands of cubic meters of petroleum contaminated soil with no cost effective treatment alternative available.

In most cases, indigenous bacteria present in petroleum contaminated soil break down petroleum hydrocarbons, which are a source of energy for the bacteria. The advantage of treating petroleum contaminated soils ex-situ is the ability to amend the contaminated soil with nutrients, bacteria and bulking agents. By amending the contaminated soil, it is possible to construct a biomound with a more conducive environment for bacterial growth, thus accelerating the breakdown of petroleum compounds in the soil as compared to natural attenuation in-situ.

Mn/DOT successfully completed a bioremediation pilot project in 1991. Following success of the pilot project, Mn/DOT used biomound technology to remediate petroleum contaminated soils at a number of sites. In 1993 the EPA expressed interest in Mn/DOT’s successes with passive aeration biomounds. With a grant from the EPA, Mn/DOT constructed biomounds with various soil amendments.

The objective of the biomound field evaluation was to measure physical characteristics within the biomounds which are necessary for bacterial growth. Biomounds with four different soil amendment combinations were constructed for the study. The physical characteristics measured were oxygen/carbon dioxide concentrations, nutrient availability, moisture, temperature and pH. Biomound samples were collected during treatment to demonstrate reduction of petroleum hydrocarbons.

In order to sustain efficient rates of hydrocarbon degradation, the biomound environment must provide certain essential elements to promote bacterial population growth. The most efficient form of hydrocarbon degradation is accomplished by aerobic bacteria. To survive, aerobic bacteria need...
oxygen, moisture and nutrients. These elements were provided in the biomound field evaluation as follows:

- **Oxygen**
  Since oxygen is consumed by aerobic bacteria during degradation, a means of replenishing oxygen in the biomound is needed. Aerobic bacteria need a minimum concentration of about 2 percent oxygen to survive. Mn/DOT uses a passive aeration system to supply oxygen to the biomound. Figure 1, right, illustrates the passive aeration system used in the study.

Wood chips were added to all the biomounds as a bulking agent to reduce the bulk density of the soils and enhance diffusion of oxygen in the biomound matrix.

- **Nutrients**
  Petroleum compounds alone do not supply all the nutrients required by soil bacteria. Nutrients already present in the soil vary from one soil type to another. A common ratio to determine appropriate nutrient requirements is 100 parts total carbon to 10 parts nitrogen to 1 part phosphorus. Nutrient amendments varied among the five biomounds. The control biomound received no nutrient amendment. The four remaining biomounds received either sheep manure, granulated fertilizer or a combination of these amendments.

- **Moisture**
  Moisture was increased in the biomounds by mixing moistened wood chips with the contaminated soil. Manure itself may have also been a moisture source. Bacterial degradation occurs through a range of moisture field capacities of approximately 20 to 80 percent. The optimum moisture field capacity for biomounds is approximately 40 percent. This concentration represents a balance between having an adequate supply of water in the soil matrix pore spaces without preventing effective diffusion of oxygen.

- **Temperature**
  Since bacterial activity increases with warmer temperatures, increasing the internal biomound temperature may result in higher rates of petroleum hydrocarbon degradation.

To sustain efficient degradation rates, the essential bacterial requirements discussed above must be provided not only when the biomound is constructed but also during the entire treatment process.

Therefore, it is important that biomound conditions are monitored periodically to ensure that proper conditions are maintained for bacterial growth.

In order to reduce treatment costs, Mn/DOT constructed the biomounds with the most cost.
Biomounds pass tests, from page 35

effective materials and equipment possible. The same passive aeration system was used in all the biomounds. Horizontal piping in the system consisted of 100 mm diameter flexible perforated drain tile. Vertical piping (risers) consisted of 50 mm diameter PVC. Pipe was joined with drain tile tees and PVC side cross outlets. Unions were secured with duct tape. There is no piping connection between the lower and upper horizontal pipe configurations. Any air exchange between the two horizontal configurations must take place by diffusion of air through the biomound matrix. Type T thermocouple wire and oxygen/carbon dioxide sampling tubes were placed in the biomounds. The oxygen/carbon dioxide sampling tubes consisted of 6.35 mm diameter tygon tubing inside of a 12.7 mm diameter PVC pipe. A hand held temperature recorder and an oxygen/carbon dioxide field instrument were used to collect the data. Initially, the oxygen/carbon dioxide field instrument could only quantify carbon dioxide concentrations from 0 to 5 percent. When carbon dioxide levels were observed to be greater than 5 percent, a new carbon dioxide detector was installed in the meter capable of quantifying up to 25 percent carbon dioxide.

The biomounds were covered with plastic sheeting and secured with sand bags placed around the perimeter of the biomound base. The tall vertical risers were stabilized with guy wires.

Mn/Dot trucks were used to transport contaminated soil and manure to the biomound site. A front-end loader and tractor were used to mix the soil and amendments and construct the biomounds.

Approximately 190 cubic meters of petroleum contaminated soil were excavated from the Maplewood Truck Station during removal of gasoline and diesel underground storage tanks on September 14-15, 1994. Laboratory analyses of stockpile samples detected maximum total petroleum hydrocarbons as gasoline range organics (GRO) and as diesel range organics (DRO) of 2,900 and 540 ppm, respectively. Three additional soil samples were collected from the soil pile prior to biomound construction. Analyses of these samples detected GRO concentrations ranging from 66 to 180 ppm and DRO concentrations ranging from 83 to 260 ppm.

During excavation, the greatest contaminant concentrations are usually found near the leaking tank with decreasing concentrations at greater distances from the tank. Heterogenous concentrations of petroleum contaminants are
commonly observed in excavated soil stockpiles. Five biomounds were constructed using this soil stockpile during the period of September 27 through October 6, 1994.

The biomounds were constructed on a bituminous pad. All soil and amendment mixing was accomplished with a front end loader and tractor. The contaminated soil was mixed with wood chips and manure—except biomounds A and B, which did not receive any manure—in batches consisting of approximately six cubic meters of soil. The soil was spread over the bituminous surface approximately 10 to 15 centimeters in thickness. The wood chips and manure were applied by the loader over the thinspread soil. The loader mixed the materials until the batch appeared to be homogenous. This mixing process continued until an adequate volume was generated to construct a biomound.

The biomounds consisted of three layers of mixed soil. The thickness of the lower, middle and upper layers was approximately 0.6, 0.9 and 0.5 meters, respectively. All the biomounds were constructed on top of a 0.3 meter thick wood chip base.

Biomounds B and C received application of granulated fertilizer. A hand operated broadcaster was used to apply the fertilizer after completion of each of the three biomound layers.

Wood chips were added to all the biomounds to improve permeability of the soil matrix. The mixture ratio was four parts soil to one part wood chips, with one exception. Soil left over after completing construction of biomounds A through D was used to construct biomound E. Biomound E was mixed with two parts soil to one part wood chips. The volumes of biomounds A through D ranged from about 37 to 43 cubic meters. Biomound E was approximately 88 cubic meters.

Aside from the addition of wood chips, the five biomounds were composed of the following:

1) Biomound A was the control for the study. No nutrient additions were introduced to the biomound.
2) Biomound B included addition of 17-17-17 NPK (nitrogen:phosphorus:potassium) granulated fertilizer at a rate of approximately 0.6 kilograms per cubic meter of soil.
3) Biomound C included addition of sheep manure at a ratio of four parts soil to one part manure. 17-17-17 NPK granulated fertilizer was applied at a rate of approximately 0.6 kilograms per cubic meter of soil/manure mixture.
4) Biomound D included addition of sheep manure at a ratio of four parts soil to one part manure.
5) Biomound E was mixed the same as biomound D except that the content of wood chips was doubled.

A similar passive aeration system was used in each biomound. The aeration system consists of two independent piping arrays. The bottom horizontal piping array was located between the lower and middle biomound layers. The bottom pipe array was connected to 6 meter vertical risers. The top horizontal piping array was located between the middle and upper biomound layers. The top pipe array was connected to shorter, 1.2 meter vertical risers.

Type T thermocouple wires were placed within the lower and middle layers of the biomounds to monitor internal temperature. Three temperature monitoring points were installed in Biomounds A through D. Four temperature monitoring points were installed in Biomound E. Periodically, some of the thermocouple wires had to be repaired, so there were occasions when temperature readings could not be collected from all the temperature monitoring points.

Air sampling ports consisted of 6.35 mm diameter tygon tubing inside of a 12.7 mm diameter PVC.
Biomounds pass tests, from page 37

The end of the PVC sleeve placed within the biomound was perforated to allow collection of gas samples. Two air sampling points were installed in Biomounds A, B, D and E. Air sampling points were located at mid-depth in the lower and middle biomound layers. Biomound C had three air sampling points. An additional air sampling point was located at mid-depth of the upper layer of biomound C.

State regulators in Minnesota require that petroleum contaminated soil piles and biomounds be covered with plastic sheeting to control runoff from the piles and prevent further volatilization of petroleum contaminants. To facilitate in covering the biomounds, the tall riser consisted of two lengths of PVC pipe. The lower length of pipe extended just above the maximum height of the biomound which allowed for easy placement of the plastic cover. Once the cover was in place, the upper length of PVC pipe was attached to complete the tall riser. The tall risers were secured with guy lines.

Sand bags were placed around the perimeter of the biomound and a system of tires and ropes secured the cover. Moisture and heat loss from the soil matrix are minimized by covering the biomound with plastic sheeting.

Temperature measurements, and oxygen and carbon dioxide concentrations were collected from the biomounds approximately once a week. Biomound E oxygen and carbon dioxide readings for the period of March 15 to May 17, 1995 are suspect because of extensive vandalism to the sampling points.

Three samples were collected for moisture and total petroleum hydrocarbon analyses from biomounds A through D at approximately one month intervals from the time the biomounds were constructed until January 1995. Samples could not be collected in January because the biomounds were frozen. The final sampling event was in April 1995.

The samples were collected with a hand auger from the same approximate locations during each sampling event. The sampling depths were approximately 0.6 to 0.8 meters. Figure 2, above, illustrates sampling locations and overall dimensions for each biomound.

Ratios of total carbon to nitrogen were determined and pH measurements collected during biomound construction and during the final sampling event in April 1995.

Oxygen and carbon dioxide measurements were collected from the lower and middle biomound layers on each biomound. Measurements were also collected from the upper layer in Biomound C. Carbon dioxide concentrations increased as oxygen levels decreased in each biomound.

The biomounds with manure additions produced the greatest depletions of oxygen in the lower regions of the biomounds. This suggests that the greatest microbial activity took place in biomounds with manure amendment. Minimum oxygen concentrations ranged from 0.5 percent in Biomound B, to 4 percent in Biomound D with manure amendment during times of peak carbon dioxide production. Minimum oxygen concentrations ranged from 10 to 13 percent in biomounds without manure.

Production rates of carbon dioxide were similar in all the biomounds. However, peak production measurements of carbon dioxide could not be quantified for the biomounds because the concentrations exceeded instrument detection capabilities.

Comparisons of production rates of carbon dioxide and depletion of oxygen between biomounds may not be completely valid since the aeration systems in biomounds B, C and E were vandalized to varying degrees. The aeration systems in biomounds A and D were not vandalized. Minimum oxygen concentrations were 13 percent in Biomound A and 3 percent in Biomound D. These concentrations are greater than the minimum oxygen requirements to support aerobic microbial activity.

Organic carbon to nitrogen ratios and pH values were determined at the beginning and end of the field evaluation. A desirable carbon to nitrogen ratio to support bacterial degradation in the compost mixture is approximately 100 to 10. Biomound A had the least amount of nitrogen available at the start of the study with an average carbon to nitrogen ratio (C:N) of 100:8, as compared to biomounds B through D. Biomounds B and C had average C:N ratios of 100:32.4 and 100:18.6, respectively, which was greater than the

<table>
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<th>Distance from North End (m)</th>
<th>Height above Base (m)</th>
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<td>0.6-1.2</td>
</tr>
<tr>
<td>A-2</td>
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<td>0.8-1.2</td>
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<tr>
<td>A-3</td>
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</tr>
<tr>
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<td>0.6-1.2</td>
</tr>
<tr>
<td>B-2</td>
<td>3.7-4.3</td>
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</tr>
<tr>
<td>B-3</td>
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</tr>
<tr>
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Figure two
desired ratio of 100:10. The average C:N ratio of 100:4.3 for Biomound D was slightly less than the desired ratio.

Published data of nutrient availability in sheep manure were used to calculate the necessary volume of manure amendment. Figure 3, above, depicts percentages of nitrogen, phosphorus and potassium in sheep manure. An average carbon content of 0.47 percent by weight was obtained from analyses of three soil samples before amendment additions. The carbon mass in the soil, including the maximum petroleum contamination of 2,900 ppm detected in the excavated soil, was calculated to be approximately 6.5 kilograms per cubic meter of soil.

It was assumed that 1,000 ppm carbon was present in the sheep manure, based on information provided by the EPA. The carbon mass in the soil and manure mixture was calculated to be approximately 6.8 kilograms per cubic meter of soil. The addition of manure at a ratio of four parts manure to one part soil resulted in a C:N:P ratio of 100:18:8, based on determined nutrient concentrations in sheep manure and the calculated carbon mass in the biomound mass. This nutrient concentration was greater than the desired C:N:P ratio of 100:10:1. Therefore, a smaller volume of manure could have supplied sufficient nutrients to the biomound mass. However, since the process used in blending manure and contaminated soil can not produce a completely homogenous mixture, four parts of manure were added to one part soil (resulting in a C:N:P ratio of 100:18:8) to increase the probability that sufficient nutrients would be available throughout the biomound mass. Also, past experience in constructing biomounds has demonstrated that this manure/soil ratio produces the desired range of internal biomound temperature.

Carbon to nitrogen ratio analyses for biomounds B through D following completion of the project were all less than the 100:10 ratio, indicating depletion of the nitrogen source. The final C:N ratios ranged from 100:1.6 to 100:3.6.

Besides oxygen and nutrients, aerobic bacteria require moisture to survive. During biomound construction, sealed sample containers representing 20 percent and 80 percent maximum field capacity were prepared. These preparations were used as comparisons to estimate moisture content during subsequent sampling events. Soil moisture decreased in all the biomounds over time. The lowest moisture content observed was 30 percent of field capacity in a sample collected from Biomound C.

The highest internal temperatures were measured in biomounds with addition of manure. Maximum average temperatures in biomounds without manure amendment were 21°C in Biomound A, and 23°C in Biomound B. Maximum average temperatures in biomounds with manure amendment were 43°C in Biomound C, 54°C in Biomound D and 46°C in Biomound E. Minimum average temperatures in Biomounds A through D were -2°C. The minimum average temperature in Biomound E was 1°C.

Higher internal temperatures were measured for a longer period of time in Biomounds D and E. Internal temperatures of Biomounds A and B, which did not contain manure, decreased to the point of freez ing in approximately early February and mid to late January, respectively. Internal temperatures at or below the freezing point were recorded in biomounds with manure amendment from approximately late February to early to mid March. Biomounds with manure produced internal temperatures above freezing approximately 18 to 47 days longer than biomounds

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Biomounds pass tests, from page 39

without manure.

The pH values were similar for biomounds A through D both at the start and finish of the project. Also, initial and final pH measurements in each biomound did not show significant change over the course of the study. Initially, average pH levels ranged from 7.58 for Biomound B to 8.80 for Biomound C. Final average pH levels ranged from 7.90 for Biomound C to 8.59 in Biomound A.

Final sample analyses indicated degradation of total petroleum hydrocarbons as gasoline/fuel oil (TPH) of 97 to 100 percent (100 percent degradation represents no detection of the analyte above the method detection limit of 5 ppm). Biomound D, with only manure added as a soil amendment, had a hydrocarbon degradation of 97 percent. Final analysis detected 15 ppm TPH in one sample. Biomounds A, B and C had 100 percent hydrocarbon degradation.

Samples collected in September 1994 were analyzed for total petroleum hydrocarbons as diesel range organics (DRO), Wisconsin Modified Method. At about this time, Mn/DOT began to suspect that the DRO analytical procedure was reporting “false positive” petroleum hydrocarbon results. In discussions with EPA and laboratory personnel, it became evident that organic matter present in the soil matrix, such as manure, may have resulted in false positive petroleum concentrations being reported by the laboratory.

To test for possible false positive results, Mn/DOT collected and analyzed samples of manure, uncontaminated soil and uncontaminated soil/manure mixtures for DRO concentrations. Similarly, lab analyses reported petroleum compounds present as DRO in samples containing manure. The control sample, uncontaminated soil without the addition of manure, was reported as not having petroleum compounds present as DRO, above method detection limits. Lab personnel also stated that gasoline range organic (GRO) analyses do have the potential to report false positive hydrocarbon results. Therefore, since the method was falsely reporting DRO due to the presence of the manure, Mn/DOT analyzed the remainder of samples collected during the field evaluation for total petroleum hydrocarbons as gasoline/fuel oil (EPA 8020 Modified method).

Air circulation within the biomound was probably driven by two forces. First, air movement probably occurred as a result of convection within the biomound. Internal biomound temperatures recorded in previous Mn/DOT biomound projects demonstrate that higher temperatures are produced in the lowest portion of the biomound. This results in warmer, less dense air in the bottom of the biomound. Therefore, heat produced during decomposition of organic matter could displace air towards the top of the biomound and force it through the upper pipe system.

Secondly, air circulation may also have been driven by the atmospheric difference present between the short and tall riser openings. The existence of a pressure gradient between the tall and short riser openings created a potential air flow from high to low pressure regions. The passive aeration design used during the project appeared to circulate an adequate amount of oxygen to the biomounds, including the lowest layer where degradation rates were higher, based on measured concentrations of carbon dioxide. Biomounds with aeration systems not subjected to vandalism showed oxygen concentrations equal to or greater than 3 percent. This amount of oxygen is adequate to support biomound bacterial activity. Therefore, it appears that the passive aeration system provided enough oxygen to the biomounds to support microbial activity.

In general, the carbon dioxide levels increased following construction of the biomounds until about the beginning of January when levels began to decrease. This was probably a result of decreased bacterial activity within the biomound as the interior of the compost mass cooled during the winter season. Carbon dioxide levels began increasing once again in late April, along with depletion of oxygen.

Higher concentrations of carbon dioxide and lower concentrations of oxygen were measured in the lower layer of the biomounds, as compared to the middle or upper biomound layers. This may be attributed to

Continues on page 42→
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greater rates of decomposition in the lower regions of the biomound or greater efficiency of air circulation in the upper biomound regions.

Comparisons of oxygen depletion among biomounds with and without manure demonstrate significantly higher rates of oxygen usage in biomounds amended with manure. This indicates a greater rate of microbial activity than in those biomounds without manure. This could in turn suggest a higher potential rate of hydrocarbon degradation in biomounds with manure.

Based on the desired carbon to nitrogen ratio of 100:10, nitrogen additions were adequate for promotion of bacterial populations with amendments of granulated fertilizer (Biomound B) and manure with granulated fertilizer (Biomound C). Addition of manure alone resulted in slightly less than the desired C:N ratio. Analyses of samples collected from Biomound B demonstrate the greatest amount of nitrogen available among the four biomounds at the start of the study. This is probably because the only nutrient source added to Biomound B was granulated fertilizer. Thus, the carbon content was not increased in the Biomound B mass, unlike the manure amended biomounds. Biomounds C and D experienced not only an increase in nitrogen but of carbon as well with the addition of manure.

In general, biomounds amended with manure generate greater internal temperatures than biomounds without manure. Biomounds with manure also remain warmer than biomounds without manure during the onset of cold ambient temperatures. Therefore, manure amended biomounds may have longer effective treatment times during cold weather conditions.

Biomound E retained heat generated during organic compound decomposition for the greatest length of time. This is most likely due to the larger biomound size. Biomound E also produced higher average internal temperatures during treatment than the other biomounds. This is probably due to a decreased surface area associated with the volumetric increase, thus reducing the potential for surficial heat loss as compared to the smaller volume biomounds. The size of Biomound E may represent an approximate minimum critical size, when mixing at a ratio of four parts soil to one part manure, for extending bacterial activity in cold weather climates.

The pH values were fairly consistent among biomounds and did not change significantly during the treatment period.

Moisture content decreased in all the biomounds over time. The lowest moisture content measured was 30 percent of field capacity in a sample collected from Biomound C. This moisture content, while not optimum, is adequate to support bacterial populations. The samples for moisture analysis were collected from a depth of 0.6 to 0.8 meters into the biomound.

Petroleum degradation was observed in all the biomounds including the control. Concentrations of TPH as gasoline or as fuel oil (EPA 8020 Modified method) were reduced by at least 97 percent.

Careful consideration must be given to selection of an analytical method for biomound samples. Biomound samples, especially those containing organic matter such as manure, present some unique quantitation problems when selecting an appropriate analytical method for analysis of petroleum hydrocarbons. The presence of composted manure in the samples can result in reporting of “false positive” petroleum concentrations when certain procedures are used.

According to the laboratory which performed the analyses for this study, the methodologies of total petroleum hydrocarbons as diesel range organics and as gasoline range organics are susceptible to reporting organic matter concentrations as an indication of the presence of petroleum compounds. Since Mn/DOT had originally intended to use DRO and GRO methodologies, an alternative analytical procedure had to be selected.

The soils used in the project were known to be contaminated with a mixture of gasoline and diesel fuel. Therefore, the method to be used had to detect both. Also, budget constraints prevented using more sophisticated techniques such as gas chromatography (GC)/mass spectrometry (MS) for routine analysis.
GC/MS had been used on past studies to positively confirm degradation of benzene, ethylbenzene, toluene and xylene compounds.

The direct injection technique (California Method or Wisconsin DRO Method) includes a solvent extraction that partitions the petroleum hydrocarbons from the soil matrix into a solvent system. The extraction removes other naturally occurring compounds present in the compost which are not commonly present in contaminated soils excavated from an underground storage tank leak site. Many of these compounds elute as peaks within the hydrocarbon area of the chromatogram and can be mistakenly included in the total petroleum hydrocarbon (TPH) peak summation calculation. This can result in reporting erroneously high TPH values. In addition, the extraction and direct injection procedure can result in the loss of some of the lighter petroleum hydrocarbon components. This was a concern because of the potential presence of gasoline contamination in the biomound soil.

The diesel hydrocarbon range is defined as C10 to C28 by the Wisconsin DRO method. However, this method has been established to determine a wide range of petroleum contaminants including motor oils. Diesel fuels consist of hydrocarbons in the lower end of that hydrocarbon range—typically C10 to C22. The purge and trap GC technique does not cover the entire hydrocarbon range. However, since the same analytical conditions are used for calibration using a diesel fuel standard and sample, complete recovery of the full hydrocarbon range is not critical for effective quantitation analysis. In addition, less interference from non-hydrocarbon—manure compost—compounds has been observed compared to the direct injection GC technique.

A purge and trap gas chromatography procedure (EPA method 8020 modified) was selected as the primary method of analysis for the following reasons:

1) The purge and trap procedure has been effectively able to quantitatively determine hydrocarbons in both gasoline and fuel oil in biomound studies completed over the past four years;

2) The organic compounds present in the manure compost do not interfere with quantitation to the extent that has been observed with direct injection procedures;

3) The longer chain petroleum hydrocarbons can be accounted for through the quantitation process using a standard diesel fuel as a calibration material. The fraction of diesel hydrocarbons that may not be detected by the purge and trap method are less soluble in water and thus are relatively immobile in soil as compared with lighter hydrocarbon compounds. Therefore, the risk to possible receptors in the environment associated with heavier hydrocarbon components is not as significant as the risk associated with lighter hydrocarbon components since the heavier components are not as mobile.

Biomounds amended with manure showed increased microbial activity compared to biomounds without manure. This is evidenced by greater magnitudes of oxygen depletion and greater internal biomound temperatures. This may be attributed to one or a combination of the following reasons: the manure provided not only nutrients, but additional bacteria as well which may also have consumed petroleum hydrocarbons; the manure reduced the bulk density of the soil matrix allowing for more efficient diffusion of air through the biomound mass.

The addition of manure in biomounds has resulted in Mn/DOT's beneficial rese of the soil following successful treatment. Once the soil is cleaned to regulatory standards, the composted soil is used as top soil amendment on highway construction projects. Biomounds amended with manure effectively recycle not only petroleum contaminated soil but animal waste and wood chips as well. This process has benefited producers of animal wastes, especially in metropolitan areas where disposal of manure can be difficult and expensive.

Mn/DOT will continue to use biomound technology to remediate excavated petroleum contaminated soils and plans to further investigate analytical techniques for composted soils and examine air flow within biomounds on future projects.

Write in 686 for more information
Factors to consider before adding microbes and nutrients

Take this list along when shopping for bioaugmentation

By Michael Piotrowski, Ph.D. and John Cunningham

Over the years, it has become apparent that in bioremediation, adjusting the site’s physical and chemical environment (biostimulation) is more important as adding the best site-specific microbial strains (bioaugmentation). In the early years of commercial application of bioremediation, emphasis was often placed on simply applying microbial strains with the ability to biodegrade specific organic contaminants to the affected sites. However, because the application of the strains was generally found to be insufficient by itself to induce satisfactory results, the influences of site factors on microbial activity came to be recognized as key determinants for success. At many sites, factors such as the absence of oxygen, nutrient imbalance and other physical or chemical conditions were identified as important impediments to microbial destruction of target contaminants.

This realization prompted the development of engineered systems designed to alleviate site conditions that impair microbial activity. The key advantages to biostimulation relative to bioaugmentation are lower costs for biostimulants as compared to microbes, easier subsurface delivery of biostimulants compared to delivery of microbes and easier public acceptance of biostimulation compared to adding exogenous microbes.

In the last several years, applications of biostimulation have greatly out-numbered applications of bioaugmentation. For example, in 1994, the EPA reported that 77 percent of 128 sites that the agency was tracking had selected biostimulation over bioaugmentation. Biostimulation works well, especially in cases where site adjustments are properly maintained over the course of remediation. The consensus among many bioremediation practitioners is that biostimulation is a sufficient method to decontaminate many sites.

Recently, we have received more and more reports from clients that consultants are recommending bioaugmentation at their petroleum fuel-contaminated sites—sites which can be readily treated with biostimulation. Many clients and consulting engineers do not have the background to ask the key questions to assess whether the microbial product being proposed for use at a site will be effective. So here is a checklist of questions to ask a vendor to assist in that decision.

1. What is the cost of the microbial product on a unit treatment basis?

   This should be the first question to ask to evaluate whether application of the microbial product will be cost-effective. Ask for the total cost per cubic yard (or cubic meter) of soil or gallon (or liter) of groundwater to reduce the concentration of the target organic contaminant from a starting concentration to the remedial goal.

   Verify if the product unit cost includes the labor cost for product applications and the cost for any subsequent soil manipulation. If, for example, one kilogram of just the product costs $10, and you need to apply one kilogram of product three times to each cubic meter of soil for satisfactory treatment, the cost for the microbial product alone is $30 for each cubic meter. In this example, the microbial cost to treat the soil by itself exceeds the typical cost of biostimulation as applied in a simple land treatment unit.

2. Has the microbial vendor conducted or overseen controlled experiments that demonstrate the superior biodegradative capability of the exogenous microbes compared to the indigenous microbes?

   Often, no such experiment is conducted, so there is no proof that the product will produce a higher biodegradation rate than the indigenous microbes. If the vendor has conducted or overseen such an experiment, request a copy of the research prior to ordering the product. The report should clearly outline the experimental design and the results, and provide names and telephone numbers of the researchers who performed the experiment. Key features of a properly performed experiment to evaluate a microbial product vs. the indigenous microbes include:

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• The contaminated soil batch used in the experiment should have been collected from a spill site where contamination had been present for at least several months. Be wary of studies in which the organic contaminants were added to clean soil by the researchers themselves, as this approach can be biased toward the microbial product.

• The soil batch used in the experiment should be loamy and not mostly sand. Sand typically doesn’t contain an appreciable natural microbial community, again biasing results in favor of a microbial product.

• The soil batch should be thoroughly homogenized prior to its use in the experiment.

• In the base experimental design, the soil batch should be split into two equal portions. One portion is treated with the microbial product, dechlorinated water and the vendor’s nutrient product. This is the inoculated soil portion. The second portion should receive the dechlorinated water and the vendor’s nutrient product, as the control portion.

• A minimum of two composite replicates should be collected from each soil portion immediately after the amendments are added. Those samples should be analyzed for organic contaminant content using an appropriate method. For example, EPA method 418.1 is not a good method for hydrocarbon contaminant studies because it does not produce a chromatogram that can be inspected and interpreted.

• During treatment, each soil portion should be incubated identically, preferably at temperatures near the ambient temperatures in the field.

• During experimental monitoring, a minimum of two composite replicates should be collected from each soil portion during each sampling event. Compositing the samples maximizes the probability of observing statistical differences in organic contaminant concentrations between the treatments. Soil sampling should be conducted a minimum of three times over the course of the experiment.

• The analytical results section of the report should discuss the quality of the data. Verify that a quality assurance/quality control program was used.

• The results of all the replicate samples should be presented.

• Preferably, graphs containing timelines of contaminant concentrations in each treatment over the course of the study should be presented.

• If such graphs are used to present analytical results, each mean data point on the graph should include error bars depicting the standard error around each mean value.

• If the error bars of the soil batch that received the microbial product do not overlap the error bars for the control batch during the latter stages of the experiment, the analytical results for each batch were probably significantly different, as in Figure one, page, 46. In that case, if the mean organic contaminant concentrations in the inoculated soil portion are lower than the mean concentrations in the control portion, as is the case in figure one, it would appear that the microbial product produced a significantly higher rate of contaminant biodegradation compared to the indigenous microbes. Conversely, if error-bar overlap occurs in the latter stages of the experiment, the organic contaminant concentrations in the two soil portions are probably not significantly different, and the microbial product would not appear to increase the rate of contaminant biodegradation compared to the indigenous microbes, as shown in figure two, page 47.

3. If your site is contaminated with an exotic organic contaminant, does the vendor have proof that the microbial product is effective against the compound under site-specific conditions?

One area that holds promise for bioaugmentation is the treatment of exotic or synthetic organic contaminants such as pesticides, PCBs, and dioxins. A number of microbial strains have been isolated that exhibit the ability to biodegrade such resistant contaminants. However, in a number of cases, biodegradation has only been demonstrated in the lab, and not in the field. Therefore, unless the vendor has field data proving that the microbial product can reduce the contaminant concentration under field conditions, it might be prudent to proceed with caution.

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Top 11 factors, from page 45

conditions that resemble your site, you may want to have the vendor perform a pilot-scale field study to generate data demonstrating the utility of the microbial product at your site.

4. If the vendor proposes to treat an exotic organic contaminant at your site, will special treatment conditions be required?

For some exotic organic compounds, such as highly chlorinated aliphatic or aromatic hydrocarbons (PCE, PCBs with Aroclor numbers >1242) or explosives, current research suggests that either an anaerobic approach or a sequential anaerobic/aerobic approach may be able to produce contaminant reduction. In such cases, one would anticipate that the vendor would propose to enact one of these approaches at your site. How will such special conditions be implemented at your site? The cost and time to treat site materials can be influenced by the methods proposed by the vendor to produce the special conditions.

5. Is the microbial product a monoculture or a consortium?

Initially, many commercially available microbial products contained only one strain of microbe—monocultures. While this approach was the simplest, it ignored the fact that microbes in nature exist in communities containing many strains—consortia. Two problems can develop with the use of monocultures.

First, the monoculture may not be able to compete with the naturally occurring microbes. If so, site inoculation with the monoculture would not have any influence on contaminant biodegradation rate. Second, if the monoculture does survive, it may not possess the enzymatic capability to completely biodegrade the target contaminants present at the site. In that case, metabolic byproducts may increase in concentration at the site, and concerns could arise regarding the toxicities of the byproducts. In the second case, certain target organic contaminants may not be biodegraded by the added microbes at all.

These realizations have induced many microbial vendors to develop products containing microbial consortia. The consortia presumably contain complementary strains which may aid in the persistence of the consortia at your site, and serve to completely biodegrade the target contaminant, or treat the suite of target contaminants that may be present.

6. What is the source of the microbes in the product?

How are the contaminant-specific microbes isolated and developed? Can the microbes pose human health or ecological risks?

This series of questions characterizes the nature of the microbes. A number of products contain microbes derived from sites chronically exposed to organic contamination—oil seeps, fuel-production facilities, fuel tank bottoms, for example. Such microbes are typically accustomed to elevated concentrations of multiple organic contaminants, and may be able to biodegrade a suite of organic contaminants that might be present at your site.

In other cases, microbes are developed in a laboratory using techniques designed to select microbes capable of biodegrading target organics at elevated rates and/or initial concentrations. The starting cultures for such efforts may be sewage sludge or microbial strains maintained in culture depositories. Because microbes derived from sewage-sludge starter cultures could pose a health risk to the human population in the vicinity of your site, you may wish to avoid such products.

In some cases, direct genetic engineering may be used to develop the microbial strains. In this case, due to ecological and human health risk concerns, federal, state or local regulations may preclude their use at your site. Verify that genes from different genera of microbes were not combined to produce the final microbial strains, as such microbes—known as intergeneric recombinants—are strictly regulated, and cannot be released into the environment.

7. How is the product produced, maintained and reactivated?

This series of questions is designed to identify the culture conditions used to produce the product, how it is stabilized for transport to your site, and the method required to reactivate the strains.

First, determine how the microbes are grown at the vendor’s facility. Important questions include: What
types and concentrations of organic contaminants are used to maintain the microbes? If the vendor maintains its cultures on high concentrations of diesel fuel, and your site is contaminated with gasoline, the product may not be totally effective in biodegrading the lighter organic constituents present in gasoline. Therefore, determine if the organic contaminant types and concentrations used to maintain the microbes in the laboratory resemble the contaminant conditions at your site.

Second, because it is expensive to transport water-based cultures due to the weight of the water, and because the transport of live microbes requires expensive maintenance techniques, many vendors stabilize the microbes with freeze-drying or desiccation approaches prior to transport. How long has the product batch proposed for use at the site been stabilized? What is the average shelf-life for the stabilized product? How is the shelf-life determined?

While it is well known that many microbes can persist in stabilized form for extended periods of time, the longer the product has been stabilized, the less likely most of the microbes in the batch can be reactivated. If the batch has been stabilized for a time period shorter than the shelf life, the chances are good that most of the microbes in the batch can be reactivated.

Also identify the nature of the material used to transport the microbes, the carrier. The carrier used to stabilize the microbes represents a considerable

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fraction of the total weight of the microbial product. For example, a number of microbial products are stabilized on sawdust or similar materials. Because the microbial component typically represents a small fraction of the total weight, the percentage of active ingredients of the product—the microbes—tends to be quite low. Consequently, shop around to find a microbial product with the highest percentage of active ingredient. Remember that the percentage of active ingredient value assumes that the majority of microbes can be reactivated, and this may not always be the case.

Third, determine the steps required to reactivate the microbes in the product, and who is responsible for reactivation. In some cases, reactivation may take several hours or even days. If you are responsible for reactivation, are the instructions detailed enough for you to proceed confidently? If not, get additional information.

8. How long have the microbes in the product been isolated from the environment?

The longer the microbes have been isolated from the rigors of nature and maintained in the relatively benign conditions of a laboratory, the more likely the microbes will have lost their fitness to survive and grow when introduced to your site. Avoid using microbial products whose strains have been kept in the laboratory for an extended period.

9. How are the microbes applied and who applies them?

Once the microbial product has been reactivated, it must be applied to the contaminated soil or water. Does the unit cost for the product include the labor cost for application? What equipment is used? Are equipment costs included?

If the vendor proposes to treat subsurface contamination, how are the microbes to be delivered? If by injection, what is the areal extent of effective subsurface treatment produced by the injection process. Because microbes do not tend to migrate large distances through soils, it will likely be necessary to inject the microbes across a closely spaced grid pattern to treat the areal extent of contaminated subsurface soil. In cases where there is a large area of contaminated subsurface soil on the site, numerous injections will probably be required. Also, if the contamination is considerably deep, the injection equipment must be able to access the deep layer, and deep injection can be costly.

If a vendor proposes to treat groundwater in situ, again, because microbes don’t travel very far, even in the saturated subsurface, expensive multiple injections across a closely spaced grid pattern will likely be required to treat a large dissolved contaminant plume. In some cases, a vendor may propose to inject or place the microbes in the saturated subsurface along a transect perpendicular to the direction of groundwater flow. This approach is intended to create a microbial fence to interdict the contaminant plume and deter onsite contaminant migration. While plausible, unless an anaerobic approach is proposed for exotic organic contamination, microbial injection by itself probably won’t produce an effective fence, because oxygen addition will also be required to treat most fuel hydrocarbons.

10. How many times must the microbes be applied to produce satisfactory site cleanup?

How will the need for reapplication be determined? Who pays for the reapplications?

11. Are any other actions required during site treatment?

For soil treatment, it is usually necessary to periodically till the soil, maintain adequate moisture and perhaps apply nutrients. For groundwater treatment, oxygen and nutrient delivery may be required. In addition, other actions may be necessary, such as periodic adjustments of pH levels. Because such activities add to site treatment costs, evaluate if the added cost of applying the microbial product is justified. In a number of cases involving fuel hydrocarbons, actions such as tilling, oxygen and
nutrient delivery alone will stimulate appreciable hydrocarbon reductions if properly performed.

**Nutrient addition**

Once the microbial product has been researched, of equal importance is the issue of adding nutrients to a site to enhance biodegradation. Recently more and more reports are stating that nutrient addition did not measurably enhance the rate of contaminant biodegradation at a number of sites.

Such reports are surprising in that the basic theory of biological growth holds that living organisms, including microbes, require the proper combination of carbon, nutrients, trace elements and vitamins for growth, maintenance and reproduction. Proper microbial nutrition is required for optimal enzymatic activity, intracellular transport and energy production. If those processes are not operating properly, efficient metabolism and destruction of the organic contaminant are impaired. On a broader scale, the proper application of nutrients to a site increases the rate of organic contaminant biodegradation, fosters the complete biodegradation of the contamination and improves the overall stability of the bioremediation process.

However, it is possible that the natural nutrient contents in the contaminated soils or groundwater at a number of sites may be sufficient to support considerable microbial growth, maintenance and reproduction. Consequently, nutrient additions at such sites may not provide additional benefit for contaminant reduction. However, we strongly question statements that nutrients are not required at most sites to enhance biodegradation rates.

Factors such as nutrient types, concentrations and ratios, as well as the physical means used to apply the nutrients to the soil are all critical to the successful enhancement of biodegradation rates. If one or more of the factors are not adequately addressed or implemented, nutrient addition could appear to be ineffectual in enhancing contaminant reduction.

Furthermore, while the proper application of nutrients can enhance the rate of contaminant biodegradation, improper nutrient application could actually reduce contaminant biodegradation rates. Consequently, nutrient additions can be helpful in reducing organic contaminant concentrations at a large number of affected sites, if they are applied with foresight and if they are applied with the appropriate methods.

There are at least four underlying assumptions involved with most studies of nutrient applications at contaminated sites. First, it is assumed that the method of nutrient delivery was successful in distributing the nutrients to the microbes. Second, it is assumed that microbial nutrient requirements in nature are well understood. Third, it is assumed that microbial nutrient requirements are broadly applicable. Finally, it is assumed that the nutrient formulation applied to the site was a good formula for the site’s microbes in terms of enhancing the rate of biodegradation. However, these assumptions are often faulty.

Effective delivery of nutrients to subsurface environments is not easily accomplished. Typically, nutrient delivery takes the form of surface irrigation or subsurface injection using a dilute nutrient solution. More recently, efforts have been made to inject gaseous forms of nutrients into contaminated subsurface soil zones. However, for each of these approaches, key nutrients, such as phosphorus and nitrogen compounds, tend to become immobilized before they travel appreciable distances in the subsurface. Consequently, it is difficult to achieve adequate nutrient spreading and an even distribution of the nutrients across the contaminated subsurface region.

Furthermore, few studies document efforts to verify that the method used to apply the nutrients was successful in evenly distributing the nutrients throughout the contaminated subsurface zone. The basic assumption that nutrient delivery to the subsurface is effective is rarely verified, and probably invalid.

Very little basic research is available with respect to microbial nutrient requirements in natural

Continues on page 50→
environmental. This low level of research persists, even though this information may be the key to producing rapid contaminant biodegradation.

Much of the current knowledge regarding microbial nutrient requirements for organic biodegradation is derived from observations made at wastewater treatment plants, from agricultural studies with plants, and from lab studies of microbial monocultures. These data are not adequate for even a basic understanding of microbial dynamics in the subsurface.

Studies evaluating the biodegradative responses of natural microbial communities to various combinations of nutrient additions are needed. Site-specific evaluations will continue to be required until we gain a more comprehensive understanding of critical nutrient limitations in natural environments. In most cases, site-specific preliminary analyses of nutrient balance, dynamics and microbial response to nutrient additions are either not conducted at all, or are inadequate. It is often assumed that microbial nutrient requirements established in wastewater treatment plants or in laboratories are broadly applicable. However, there is good reason to believe that microbial nutrient requirements can vary considerably from site to site.

For example, there are over 10,000 soil types recognized by the U.S. Soil Conservation Service in the U.S. alone. Each soil type has been classified according to its various characteristics, including its setting, history, climate and physical / chemical / biological aspects. It is not unreasonable to expect that many of those soil types may exhibit unique responses in terms of the influence of nutrient addition on the rate of contaminant biodegradation. Consequently, the assumption that microbial nutrient requirements for contaminant biodegradation are broadly applicable is unfounded.

The exact nutrient formulation that will enhance contaminant biodegradation at a site is also rarely assessed. The three major elements commonly required at contaminated sites to enhance contaminant biodegradation are nitrogen, phosphorus and sulfur. The most readily available sources of these elements include nitrate, urea and ammonium for nitrogen; ortho-phosphate, triple superphosphate and polyphosphate for phosphorus; and sulfate and polysulfides for sulfur. Each form of the element may exert a different response in terms of the contaminant biodegradation rate at a particular site. In addition to those three elements, there are another six major elements which may be required at a particular site to foster elevated rates of biodegradation. They are potassium, iron, magnesium, calcium, sodium and chloride.

If one were to conduct a basic screening study to evaluate: 1) the site-specific effectiveness of adding each of the nine elements on biodegradation rate, 2) the elemental concentrations required to enhance the biodegradation rate and 3) the influence of nutrient interactions on the biodegradation rate, multiple analyses of 512 experimental units would be required!

Furthermore, because the results of the study would only provide screening-level data, additional studies would be required to optimize the site-specific rate of contaminant biodegradation. Among the key nutrient aspects that would be examined in the latter studies would be the identification of the best form of each nutrient to apply.

It would be quite costly to conduct even these basic screening and optimization studies using the standard experimental protocols, and most clients would not fund such studies at their sites. Yet, without preliminary screening and optimization studies, there is no scientific basis for the selection of the appropriate nutrient formulation for application to a site.

Fortunately, there is an experimental technique that allows screening evaluations of the influences of the nine elements on the rate of contaminant biodegradation that uses only 16 experimental units. Furthermore, the subsequent optimization study would typically require analyses of only 18 experimental units.

The technique, derived from industrial optimization...
protocols, allows cost- and time-efficient evaluations of nutrient requirements, potential influences on contaminant biodegradation rates, and identifications of optimum nutrient formulations. We recently completed a laboratory study of this kind using groundwater samples collected from a gasoline contaminated site in central California.

The results of the study demonstrated that the proper nutrient formulation increased the rate of contaminant biodegradation by a factor of three, over the improper nutrient formulation and the no nutrient control, as shown in figure three, page 50. In fact, the biodegradation rates for the latter two treatments were essentially equal. Finally, the treatment using the proper nutrient formulation exhibited less variability in the rate of contaminant biodegradation compared to the other two treatments. That observation indicated that the proper nutrient formulation would also improve the stability of the bioremediation processes in the groundwater.

The results of that study highlight the importance of identifying the proper nutrient formulation for use at a site. If the improper nutrient formulation were applied to the groundwater at the California site, our empirical model based on the study results, indicated that the time required to complete bioremediation would be three times longer compared to application of the proper formulation. This is shown in figure four, above. Because a significant reduction in the time required to treat a site can produce considerable cost savings, it is beneficial to invest in such preliminary nutrient studies.

It appears that for a majority of sites where nutrient additions have been attempted, at best, inadequate preliminary evaluations of nutrient influences on contaminant biodegradation rates were conducted. Consequently, the nutrient formulations applied at many sites were likely inappropriate, and may have resulted in observations that nutrient additions did not enhance the rate of biodegradation.

A comprehensive evaluation of nutrient influences on biodegradation rates at a wide range of sites using an efficient protocol will provide considerable insight into nutrient influences on biodegradation rates, and highlight the importance of identifying the proper nutrient formulations. Write in 687 for more information.
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Time release nutrient augments bioactivity

At a recent test at the U.S. Navy facility in Craney Island, Va., E.T.20, a non water soluble, oleophilic, controlled release nutrient and selected naturally occurring bacteria strain, outperformed conventional water-soluble nutrient addition by a factor of 1.4. E.T.20, developed at Tel-Aviv University by Dr. Eugene Rosenberg, is a product of Quantum Environmental Technologies. E.T.20 introduces a source of nutrients that are only available to E.T.20 bacteria, so beneficial degraders are increased, providing high bacteria density, says the company.

New groundwater software flows in

Geraghty & Miller Inc., a Heidemij company, Denver, Colo., announces two software programs for groundwater. AQTESOLV™ analyzes aquifer data, and is now available for use with Windows95™. A new feature is its ability to analyze a pumping test with more than one observation well, and matching type curves to data from all wells simultaneously. Mod1Cad386™ is design software for numerical groundwater modeling, also available for Windows95. New features include support for transient recharge, the ability to directly import map files without transition to an intermediate format, and comprehensive electronic help, says the company.

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Environmental Chemistry for Investigating and Remediating Soil and Groundwater Contamination

Program #6884 * June 10-13, 1996

The University of Wisconsin-Madison, Department of Engineering Professional Development will offer a course, Environmental Chemistry for Investigating and Remediating Soil and Groundwater Contamination, on June 10-13, 1996.

For more information:
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Training opportunities
Sharpen your pencils


- California Environmental Protection Air Resources Board, Compliance Division, offers a variety of courses throughout the year, including such titles as: Solvent Cleaning, Hot Mix Asphalt Facilities, Asbestos Demolition, VOC Controls, Soil Decontamination. For a schedule and fee information, fax a request to 916-445-5745, or phone 916-322-8272.

- Construction Estimating Institute of America, a non-profit educational institution in Sarasota, Florida, offers a two day course, “Profit & Efficiency Techniques that Work,” designed for Florida contractors requiring continuing education units in order to renew their license. The course is offered in major cities across the country. Call 800-423-7058 for more information.

- Excel Partnership Inc. offers a one day course, Management Understanding of ISO 14000 on June 5 in San Francisco. Cost is $395. Also in San Francisco on June 17-19, is Developing and Implementing Environmental Management Systems. Cost is $995. Call for enrollment information, 800-374-3818.


- Georgia Tech Research Institute offers a variety of environmental, safety and health training programs, including OSHA Voluntary Compliance, July 8-12 in Tampa, Florida, cost $625. On September 16-20, Hazardous Material Control and Emergency Response, $900, in the Space Science Building on the Georgia Tech campus in Atlanta. Also on September 16-20 on the campus, is Management of Underground Storage Tank Systems, $795. For course information, call 404-894-7430. To register, call 404-894-2400.

- Government Institutes Inc. offers the Advanced RCRA Course, June 17-19 in Hilton Head, S.C. Cost is $999. Call 301-921-2545 for registration.

- The Major Industrial Accidents Council of Canada will hold a conference and trade exhibit November 5-6 at the Edmonton Hilton, Edmonton, Alberta. The theme of the gathering is to combine prevention, preparedness and response to industrial accidents with process safety and loss management. For exhibition information, call 613-232-4435.


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• The National Registry of Environmental Professionals offers the NREP Registered Environmental Manager and Certified Environmental Auditor workshop and exam June 6-7 in Chicago, June 20-21 in Boston, July 11-12 in Pittsburgh, August 8-9 in Salt Lake City, August 22-23 in Cincinnati, September 12-13 in Denver, September 26-27 in Newark and October 24-25 in Portland. Cost is $595. To register, call 770-486-9253.

• The Nielsen Environmental Field School Inc. offers Assessment and Remediation of Petroleum Hydrocarbon Releases, June 3-6 in Columbus, Ohio. On June 25-28 is Complete Groundwater Monitoring Field Course, and Environmental Drilling and Monitoring Wells, both in Columbus. And June 27-28, is Planning and Conducting Groundwater Sampling Programs, in Columbus. Call 614-965-5026 for fees and information.

• Oklahoma State University offers Design of Stormwater, Sediment and Erosion Control systems, August 6-9 in Oklahoma city. Cost is $375. Call 405-744-5714 for information.

• Princeton Groundwater offers the Princeton Remediation Course, June 3-7 in Orlando. Call 813-855-6898 for fees and registration information.

• Tricipe IV, trade show and conference will be August 7-8 in Pasco, Wash., near the Hanford Site. For exhibition information or to register, call 541-385-8964, or e-mail tricipe@teleport.com. For additional information, visit Tricipe's home page on the World Wide Web at http://www.teleport.com/~tricipe.

• The University of Wisconsin, Madison offers #6484 Environmental Chemistry for Investigating Soil and Groundwater Contamination, June 11-13 in Madison. Cost is $695. On June 24-26 is Horizontal Wells for Remediation, cost is $795. Call 800-462-0876 for information.

• Wright State University, Dayton, Ohio, offers a 22 week Groundwater Hydrology course through the Interactive Remote Instructional System starting July 15. Call 513-873-3648 for information.

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Write in 048
Soil & Groundwater Cleanup May 1996 55
Soil pores dictate permeability

*Studied pore characteristics to predict movement of fluids*

By Alfred Conklin, Ph.D.

Permeability is the ease with which liquids, gases or roots pass through soil. Permeability depends on and is a measure of the average characteristics—mostly size and shape—of the soil pores. Permeability data can be used to predict how long it will take to move a certain volume of fluid through a soil profile and thus, how long it will take to remediate.

In discussing permeability, the term ‘fluid’ is used to refer to either a liquid or a gas. We may be interested in either the movement of water or air or both. Soil may be washed with water or a soap solution, or it may have air blown through it. Both water and air are fluids. In this article, we will only address the movement of water through soil that is saturated with water.

Soil scientists treat soil water and soil air very differently. Water moves through and air moves in and out of soils. Water moving through soil leaches components out of the profile. It can do this when the soil is saturated or unsaturated with water. The two cases lead to different rates of leaching. Air moves in and out of soil. Oxygen is removed from soil by roots and organisms. At the same time, carbon dioxide is released into soil air. Thus, the activity of soil water and soil air are very different.

Total soil porosity can be determined by making a soil bulk density measurement. The soil bulk density divided by the particle density yields the percent solid space of soil. Solid space subtracted from 100 gives the percent void space, or the pore space. Unfortunately, this number does not provide all the information needed to understand soil porosity. This also does not reveal the data needed to understand the movement of a fluid through the soil.

Pores in soil are often defined as being one of two types. Macropores are larger, and micropores are smaller than 0.06 millimeters in diameter. This is an arbitrary, although useful designation. Fluids move rapidly through macropores, such as those found in sand. Movement of fluid is slow or very slow in micropores which predominate in clay and clayey soils. The most useful information to have is the amount of each type of pore in a soil, but this information is difficult to obtain—so difficult, that it is rarely attempted.

Most often, as a first step in trying to understand the pores in soil, an analogy is drawn with capillaries. That is, one can observe how a fluid is held or moves through glass capillary tubes of various sizes. There are three reasons this analogy rapidly breaks down when applied to soils. First, the walls of the capillaries in soil are not smooth, they are very rough and irregular. Second, the continuous pores are not straight, and finally, some of the pores in soils have dead ends.

Because of these shortcomings, a better approximation is to study the movement of water through a uniform sandy soil saturated with water, as in figure one, right. The volume of water $Q$ flowing through such a water-saturated, packed sand column is described by equation one:

$$Q = \frac{K_s A \Delta P}{L}$$

where $A$ is the cross section area, $\Delta P = P_2 - P_1$, or the pressure differential across the length, $L$, of the soil column. $K_s$ is the saturated hydraulic conductivity.

It is instructive to consider two situations. In both, there is a column of water 10 centimeters deep over a column of soil which is 100 centimeters long ($L=100$). In one case, the column is placed horizontally and in the other it is placed vertically, as in figure one. In the horizontal column, the 10 cm of water produces only 1/11th as much water flow as occurs in the vertical column. This is because the water in the vertical column is subjected to a much larger pressure difference due to the pull of gravity. This explains why water in soil almost never flows horizontally. When it does, it does so over short distances or because of a restrictive lower layer.

The $K_s$ is often used to describe and compare soil permeability. Its usefulness stems from the fact that it is easy to measure. Simply make a column of soil, saturate it, place a layer of water on the column and note the time it takes for the water to drop a certain distance. Equation two is used to find the $K_s$:

$$K_s = \frac{L}{t_1} \ln \frac{b_1 + L}{b_1}$$

*Alfred Conklin, Ph.D., is a professor in the agriculture department of Wilmington College, Wilmington, Ohio*
where $L = \text{length of the column}$, $T_1 = \text{time at which measurement is made, usually in days}$, $b_1 = \text{depth of water at the beginning or at t = 0}$, and $b_2 = \text{depth of the water at t_1}$.

Soils usually have horizons—layers of different characteristics. These differences include different $K_c$. When studying or measuring the $K_c$ of a soil profile, we are actually measuring the $K_{eff}$ or the effective $K$. This depends on the $K_c$ of each layer and its length, as shown in figure two, right. In equation three, we would sum the lengths of each layer of soil that has a different $K_c$. Likewise we would sum each of the lengths of each layer after dividing it by the respective $K_c$. The final division gives the $K_{eff}$:

$$K_{eff} = \frac{L_1 + L_2}{L_1 + L_2} \frac{K_{s1}}{K_{s2}}$$

In the field, soil permeability is estimated with a similar procedure. A hole is dug and filled with water. Water is added until rapid infiltration ceases. The soil is assumed to be saturated at this point. The hole is then filled with water, and the rate at which it infiltrates into the soil is measured. This measurement is assumed to measure saturated flow down through the profile. Horizontal movement is not considered in this procedure. Permeability measured in this way is not accurate enough to be called a $K_c$ or $K_{eff}$. Thus, it is simply reported as permeability in centimeters per hour or in inches per hour. The larger the number, the more permeable the soil. This is the type of permeability reported in soil surveys.

Soils with different textures and different compaction have different permeabilities in the field. Coarse sandy and sandy soils have more rapid—15 cm per hour—to very rapid—50 cm per hour—permeabilities. Clay soils and compacted clay soils have slow—0.5 cm per hour—to very slow—permeabilities. Loam soils with good structure may have moderate permeability of 5 cm per hour.

Good permeability is achieved by the presence of macropores. Macropores are produced by increasing the organic matter in soil, and by growing sod type crops such as grass. Mikropores are produced by working soil when it is too wet or too dry. Frequent traffic also creates micropores.

All the above assumes that all pores are open at both ends—open pores. However, in soil, some pores are closed at one end—closed pores. Under saturated conditions, all pores are full of water. Water and pollutants move through open pores by mass flow. For pores open at one end, water and pollutants can only move in or out by diffusion. Diffusion is a much slower process than mass flow. For example, in the case of a dry soil which is flooded with contaminated water, as the water moves into the soil, both the open and closed pores fill. Then, if an attempt is made to wash the soil with clean water or water containing a surfactant, at first there is a rapid removal of the contaminated water. This is followed by a slow release of low levels because it is diffusing out of the closed pores into the water flowing through the open pores. This is a slow diffusion controlled process. Thus, remediation generally shows an initial rapid phase, followed by a slow phase. One advantage of bioremediation is that it can take place within the pores, so the diffusion process is not necessary to remove the pollutant. This assumes that the decomposition products themselves are not hazardous.

Understanding the appropriate constants enables one to predict the movement of water through soil. If we know the solubility of a pollutant, its movement can be predicted, making a study of permeability of soil essential in any remediation effort. More information about permeability can be found in Soil Physics, by William Jury e.al., John Wiley & Sons Inc. The movement of water under unsaturated conditions and the movement of gas through soil will be discussed in future articles.
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Here's How It Works...

Enviro Products Inc. Investigator™

- Enviro Products Inc., of Lansing, Mich., says their Investigator™ wireless oil and water interface probe is the first wireless telemetric probe that measures the level and thickness of free product on groundwater in 50 mm or larger wells. The transmitter probe sends informational signals via a standard measuring tape to a receiver at the surface. The system consists of a micro-processor controlled interface probe, a standard 30 or 50 meter measuring tape and a receiver and display panel. The probe uses a thermal sensor to detect the presence of free phase product—diesel fuel, gasoline, kerosene, jet fuel, heating oil and most other refined fuels—and a conductivity type sensor to detect water level. The thermal sensor is accurate to ±0.76 mm. Once the sensor detects liquid, the interface probe sends an informational signal, specific to the type of liquid detected, over the entire length of the measuring tape. The transmitter has a range of 50 meters. The signal is received, decoded and processed by the receiver. The battery-operated receiver portion is controlled by processing circuitry which detects and decodes the signal from the probe. Upon decoding the signal, the circuitry activates the indicator lights and audible signals on the display panel of the receiver. The product interface measurement is derived by noting the measuring tape reading upon activation of the “free product level” indicator light with its corresponding audible tone, and again noting the tape reading when the “water level” light and tone activate. The tape is marked in 1 mm increments on one side, 0.01 foot increments on the other side, and free product and water levels can be measured at an overall accuracy of 3 mm. The tape is nylon coated steel, and is widely available at sources nationwide, and is easily replaced in the field, says Enviro Products.

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- BioActive Remediation Technologies, the in situ soil and groundwater cleanup division of Active Environmental Technologies Inc., Mt. Holly, N.J., has developed a series of Bio Logic control centers to control various liquid and air amendments for a variety of in situ remediation applications. Once a contaminated zone is identified, characterized and analyzed, BioActive provides technical support for design of a treatment system using underground piping and wells. The piping is manifolded to the control center. Water, air, fertilizer, nutrients, heat, bacterial cultures and oxidants (including hydrogen peroxide) are fed into the water stream at controlled rates, using multi-zone timer control systems. Any number of liquid amendments can be fed directly into the treatment system via venturi type, flow controlled extraction valves. Typically, three to five sources are required, and are fed on a predetermined schedule by internal or external tanks with locking fillcaps. Each unit also provides external filter loops for both air and water that has been extracted from the site, and may require batch processing, carbon filtration, air sparging or biofiltration prior to reinjection or release. Flow rates range from 1.2 to 21 cubic meters per minute. Flows of air and water can be pulsed and timed to operate at any interval. Remote sensor technology is used to program multi-zone control centers for long term site maintenance. The units can be programmed to enhance bioremediation, vapor extraction, soil venting, air sparging, soil washing and groundwater pump and treat systems. The systems typically operate 12 to 18 months to clean up in situ, but heavier soils and/or excessive contaminants as at larger industrial sites can take longer. Models are available for residential size jobs up to unlimited scale by using multiple units.

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