



Underground Tank Technology Update

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Comments and suggestions are welcome and may be directed to [John T. Quigley](mailto:quigley@epd.engr.wisc.edu) (quigley@epd.engr.wisc.edu), Project Director, 432 N. Lake St., Madison, WI 53706. Tel 608-265-2083. To comment on an article, or to suggest topics for *UTTU*, please e-mail [Pat Dutt](mailto:pdutt@twcny.rr.com) (pdutt@twcny.rr.com) or call 607-272-3212.

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Hydrocarbon biostimulation and bioaugmentation

Soil contamination at a former meteorological and radio station in Northern Quebec, Canada, had TPH (C₁₀-C₅₀) levels ranging from 1,700 to 10,000 mg/kg (dry soil). This level exceeded the government's criteria for residential sites, 700 mg/kg (dry soil), and the criteria for commercial/industrial sites, 3,500 mg/kg (dry soil). Researchers sought to clean up the site using bioremediation, but before deciding which bioremediation technology to implement, they examined the soil and contaminants (Yerushalmi and others, 2003).

Soil characteristics, toxicity assays and tests

The soil at the site is medium to coarse sand grading into sand and silt. Soil density was 2.2 g/ml while average organic content was 4.3 ± 0.3 g/kg (dry soil). Metals present in the soil included the following:

- aluminum, 1,900 to 3,000 mg/kg soil
- calcium, 1,100 to 1,700 mg/kg soil
- iron, 6,100 to 7,100 mg/kg soil
- magnesium, 880 to 1,300 mg/kg soil
- titanium, 520 to 600 mg/kg soil

Analyses also showed the presence of polycyclic aromatic hydrocarbons, ethylene glycol and PCBs. Researchers identified microbial activity by enumerating total heterotrophic bacteria.

Researchers performed the following toxicity assays:

- Microtox
- barley seedling emergence and growth inhibition
- earthworm mortality

Other tests performed included

- biodegradation activity tests
- radioactive mineralization tests

Bioremediation limitations and techniques

Bioremediation is a site-specific process. Limiting factors include

- contaminant type and concentration
- indigenous microbial population
- availability of nutrients and electron acceptors
- pH
- temperature
- soil moisture content

Researchers investigated two specific bioremediation techniques, bioaugmentation and bioslurry treatment systems, with respect to the factors above. Descriptions of the techniques follow.

Bioaugmentation. "Soil bioaugmentation is a solid-phase process where specific seed microorganisms are added to soil to enhance its biological activity. The seed microorganisms are often developed through an enrichment process. This procedure results in the selection of the most efficient microorganisms that possess the necessary metabolic pathways and enzymatic system for contaminant degradation (Cookson, 1995 in Yerushalmi and others, 2003). Soil bioaugmentation is more effective when the soil is not nutrient deficient, and the indigenous microbial population lacks the required activity or metabolic capability. However, this technology has a limited capacity if the bioavailability of contaminants, controlled by their desorption from soil, is the rate-limiting step in bioremediation."

"During the present study, the contaminated soil was amended with the developed enrichment culture and was stimulated by the addition of nutritional supple-

ments (1 ml fertilizer solution added to 220 g soil) and pure oxygen. The experiments were performed at 10°C in 500-ml Erlenmeyer flasks and shaken in a wrist-action shaker for the entire duration of tests, which lasted for 60 days. The soil inside the flasks was manually mixed daily to ensure homogeneity and to maximize soil oxygenation. The soil used in the control system was irradiated by gamma ray to eliminate its biological activities. All experiments were performed in triplicate. Soil samples were withdrawn at predetermined intervals and were analyzed for their content of TPH."

Bioslurry process. "The bioslurry treatment system consists of a mixture of soil in water maintained in a stirred reactor... [Bioslurry treatment] enhances the availability of contaminants, electron acceptors, and nutrients to the microbial population and offers the most suitable conditions for the treatment of contaminated soil, especially when mass transfer limitations control the rate of contaminant biodegradation by the microbial biomass (Zappi and others, 1996 in Yerushalmi and others, 2003). The reduction of contaminant concentration in soil is considerably higher in bioslurry reactors compared with that observed in solid-phase reactors because of the increased solid-liquid mass transfer. The improved homogeneity and increased flexibility of operation, as well as an enhanced control over the system operation, make the bioslurry the most efficient treatment technology for contaminated soils" (Yerushalmi and others, 2003).

Researchers carried out nonradioactive, aerobic microcosm tests "to simulate various bioslurry conditions and to define the most effective biotreatment system for TPH removal from soil. These tests were carried out at a higher temperature of 20°C to eliminate temperature as a limiting factor and to determine the potential for hydrocarbon biodegradation in the contaminated soil. All of the studied treatment conditions used 5 percent soil slurry in phosphate buffer solution. Gas-tight, 120-ml serum bottles with a working volume of 45 ml, used as

the bioslurry reactors, were shaken at 100 rpm on an orbital shaker in the dark for 45 days. The headspace of the bottles was sparged with pure oxygen to ensure a sufficient supply of oxygen during the entire process. Several treatment conditions were evaluated to obtain information on the rate and extent of hydrocarbon removal and to determine the most favorable condition for hydrocarbon biodegradation" (Yerushalmi and others, 2003).

Treatment microcosm conditions included use of

- contaminated soil with a nonionic surfactant, nutritional supplement and enriched biomass
- contaminated soil with an anionic surfactant, nutritional supplement and enriched biomass
- contaminated soil with nutritional supplement and enriched biomass, no external surfactants
- irradiated soil without addition of surfactants, enriched biomass or nutritional supplement (the control)

The microcosms were periodically examined for TPH in the aqueous and soil phases. Researchers estimated "extent of hydrocarbon mineralization from the amount of carbon dioxide produced as a result of the complete mineralization of hydrocarbons. The theoretical ratio of mg CO₂ produced to mg hydrocarbons mineralized was calculated from stoichiometric relationships for oxidation of petroleum hydrocarbons with the following composition:

- alkanes, 20.0 percent
- alkenes, 2.0 percent
- mono-aromatics, 27 percent
- naphthalenes, 3.5 percent
- cycloalkanes, 40 percent
- polyaromatics, 7.5 percent

The estimated value of the above ratio was 3.2. The

change of fuel composition had only a minor impact on the estimated value of this ratio" (Yerushalmi and others, 2003).

Test results

Microtox assays showed a low level of toxicity in the contaminated soil leachates. The radioactive mineralization tests indicated "that biostimulation of soil had a positive effect and increased the efficiencies and rates of mineralization of aliphatic and aromatic compounds." Biodegradation activity tests showed that the contaminated soil had a low capacity for biodegradation of petroleum hydrocarbons. Supply of nutrients did not increase the removal efficiency. "The activity tests were carried out without any bioaugmentation and the biodegradation activities were attributed to the indigenous microbial population in the contaminated soil. The abiotic removal of hydrocarbons was 6.8 percent, leaving 13.6 percent elimination due to biological degradation" (Yerushalmi and others, 2003). Researchers suggested that the low hydrocarbon removal efficiency, despite a high mineralization capacity for naphthalene and low toxicity of soil leachates, indicated the following:

- the microbial consortium does not have the enzymatic diversity required to degrade all of the contaminating hydrocarbons in soil
- the hydrocarbons in soil are recalcitrant and resist further biotransformation
- the hydrocarbons are strongly sorbed to the soil matrix, rendering them inaccessible for microbial degradation

Results of soil bioaugmentation and bioslurry studies

TPH removal efficiency was 49.2 percent after 60 days; more than 79 percent of the overall TPH removal occurred during the first 15 days. Abiotic removal was 23.1 percent, while 26.1 percent was eliminated

by biological action. "The slight increase of removal efficiency [of TPH] in the solid-phase bioaugmentation treatment system with the addition of seed microorganisms and nutrients showed the possible deficiency of the unsupplemented (original) soil with respect to these parameters."

As a solid-phase technology, bioaugmentation suffers "from mass transfer limitations that control the transfer of contaminants from soil to the aqueous phase." In addition, "Diesel fuel is known to have a low bioavailability due to sorption to the minerals and humic fraction of soil."

Overall removal for the bioslurry treatment was 70 percent after 45 days of incubation. "This increase was possibly due to the increased transfer of contaminants from the soil surface to the aqueous phase and their enhanced dissolution rate that increased the bioavailability of contaminants to the microbial culture. An increased biological activity was apparent as evaluated by an increase in the production of carbon dioxide in the headspace of the experimental bottles, demonstrating that petroleum hydrocarbons were mineralized." Yerushalmi and others (2003) also report that the "presence of surfactants, both ionic and nonionic, increased their dissolution rate in the aqueous phase as indicated by the increased initial liquid-phase concentration of TPH when compared with the control system." The increased contact of contaminants with the microbial population in soil enhances biodegradation.

Conclusions

The authors conclude that

- "the remarkable increase of the biodegradation rate in the slurry reactors, compared with that observed in the bioaugmented and biostimulated soil, indicated that TPH sorption of soil was the limiting factor controlling contaminant biodegradation"

- “the considerably higher water-to-solid ratio and thorough mixing in the slurry system, combined with the presence of surface active compounds, increased hydrocarbon dissolution rate; these factors thus increased the rate of mass transfer to the liquid phase and improved the bioavailability of contaminants to microorganisms” (Yerushalmi and others, 2003)
- increasing temperature may have increased biodegradation rate by increasing hydrocarbon solubility and degree of distribution
- adding surfactants “reduced the initial adaptation period...making the contaminants more available to the microbial population... In the present study, the use of external surfactants was not necessary because the microbial culture may have produced biosurfactants, and the addition of external surfactants to the experimental system did not increase the overall efficiency of contaminant biodegradation”
- “addition of adapted bacterial culture to soil (bioaugmentation) showed a limited increase in overall hydrocarbon removal efficiency”; however, “addition of microorganisms can accelerate the initial phase of biodegradation and can be advantageous when the contaminants have a toxic effect on the indigenous microorganisms”; in other cases “bioaugmentation with adapted indigenous microorganisms had little or possibly negative effects on biodegradation of diesel fuel in a contaminated sand”

Yerushalmi and others (2003) contend that “Although the soil bioslurry process showed an enhanced removal of contaminating hydrocarbons, further studies are still needed to optimize the process and assess its applicability for treatment of the contaminated site. These studies should investigate the effect of environmental parameters on the production of biosurfactants by the

indigenous microbial population since the formation of biological surfactants was shown to improve hydrocarbon biodegradation during the bioslurry treatment process. The overall efficiency of hydrocarbon removal and the kinetics of bioslurry process at the conditions of the site must be determined for a proper design of full-scale treatment technology” (Yerushalmi and others, 2003).

Reference

Yerushalmi, L., Rocheleau, S., Cimpoia, R., Sarrazin, M., Sunahara, G., Peisajovich, A., Leclair, G. and S.R. Guiot, “Enhanced Biodegradation of Petroleum Hydrocarbons in Contaminated Soil,” *Bioremediation Journal*, Vol. 7, No.1, 2003; <http://www.sciencedirect.com/science/journal/10889868>



Fractured rock characterization and monitoring techniques

Because fractured-rock aquifers underlie 50 percent of the contiguous United States, groundwater regulators must be aware of the techniques to monitor and characterize these groundwater resources.

Most fractured-rock aquifers, which can consist of sedimentary, igneous or metamorphic rock, typically occur within major mountain ranges. Of the 28 groundwater regions into which Health (1988; Geological Society of America, Boulder, Colorado) divided North America, 11 regions are underlain by mountainous areas of fractured-rock hydrogeologic settings. “Six of the regions (Western Mountain Ranges, Columbia Lava Plateau, Sierra Madre Occidental, Sierra Madre Oriental, Sierra Madre del Sur and Faja Volcanica Transmexicana) occur along the western edge of North America. Three regions (Northeastern Appalachians, Appalachian Plateaus and Piedmont and Blue Ridge) occur along the eastern edge of Canada and the United States.

The other two are the West Indies and the Hawaiian Islands” (Wireman, 2003).

Groundwater flow in fractured rock

Groundwater flow in fractured rock is controlled by permeable “preferential” pathways. Pathway characteristics include

- spacing
- aperture size and length
- orientation
- connectivity

Discontinuities in fractured rock facilitate groundwater flow and include

- joints
- fractures
- foliation
- faults
- shear zones
- geologic contacts
- bedding planes

Structures such as dikes and faults can also be barriers to groundwater flow. Other groundwater flow factors include fracture wall roughness and degree, and non-parallelism of walls.

Yet despite this knowledge, the need exists to “develop a more appropriate approach to characterizing the occurrence, movement and chemistry of groundwater within fractured-rock settings. There is a concurrent need to develop more appropriate methods and tools for characterizing contaminant transport in fractured rocks and selecting, designing and operating remedial technologies at groundwater contamination sites.”

Conceptual understandings

In the typical fractured-rock geologic setting, snowmelt can be a significant seasonal event, and interflow may be a dominant process during snowmelt flux. "Below this zone, groundwater flow occurs predominantly in individual fractures, fracture zones, faults, fault zones and other structural discontinuities. The rock matrix plays a minor role in groundwater flow and typically has low porosity and permeability. As a result, groundwater flow in these settings is highly preferential and controlled primarily by the spacing, orientation, hydraulic properties, and connectivity of the permeable discontinuities" (Wireman, 2003).

This setting is also characterized by

- high hydraulic gradients along preferential pathways, which can result in high groundwater flow velocities
- groundwater flow that is toward valley bottoms
- strong upward gradients, common in bedrock underlying mountain valley bottoms
- topographic drainage basins that are not always coincident with groundwater flow divides
- seasonal groundwater levels in fractured-rock aquifers that vary from 5 to 30 m because of low porosity and storage
- groundwater divides that can shift seasonally
- hydrogeologic conditions that can produce temporally and spatially dynamic groundwater flow systems

Accurate portrayal of these systems suffers from problems with fracture-scale hydraulic data collection and interpretation. Understanding hydraulic conductivity and permeability is essential. "The hydraulic conductivity through a fracture is directly proportional to the aperture width and inversely related to normal stress and depth. Fracture permeability is affected by rock temperature,

cementation, infilling and chemical and physical weathering. In fractured-rock settings, it is important to distinguish between the hydraulic conductivity of a fracture, the hydraulic conductivity of the rock matrix, and the hydraulic conductivity of a rock mass" (Wireman, 2003).

Characterization tools

Wireman advises using a number of tools and data sets ("multiple lines of evidence") to evaluate the following:

- groundwater storage and flow development
- groundwater/surface water interaction
- chemical isotopic, and biological quality of groundwater and surface water
- contaminant transport

Characterization tools include the following:

- hydrogeologic mapping
- aquifer tests
- groundwater tracing
- environmental isotopes
- borehole geophysical methods
- groundwater flow models

Hydrogeologic mapping. Traditional maps (depth to water, water table/potentiometric surface, spatial distribution of hydraulic properties, spatial/temporal distribution of water quality) need to be supplemented with maps of rock type and distribution, orientation of geologic discontinuities, and other maps related to surface water hydrography and hydrology, other nonfractured rock aquifers, and meteorological elements.

Aquifer testing. Researchers using this tool must consider test purpose and design, data type and data analyses. To measure hydraulic conductivity, field workers can use a Standard Lugen packer test or a Modified Lugen packer test and/or a tracer-injection test. "For fractured-rock aquifers that have significant matrix porosity (low

matrix hydraulic conductivity) and regularly spaced fractures (high hydraulic conductivity), pumping test data can be used to estimate hydraulic characteristics of the fractures and the matrix blocks. Double porosity models assume that porous media flow occurs within the matrix block and within the fractures" (Wireman, 2003).

Groundwater tracing. This tool can "be used to delineate groundwater flow paths, determine groundwater flow velocities along the delineated flowpaths, and help estimate mass loading to a stream along a preferential groundwater flow path" (Wireman, 2003). Tracer recovery and groundwater flow data when analyzed together can provide quantitative data for evaluating contaminant behavior and fate. Wireman gives more information in his paper on tracer types and applications.

Environmental isotopes. Isotope data (which includes isotopes of hydrogen, oxygen, carbon, sulfur and nitrogen) can help to characterize groundwater recharge sources in fractured-rock settings. Because of fractionation processes, environmental isotopes become fingerprints of recharge water.

Borehole geophysical methods. Borehole geophysical methods typically include caliper fluid logs, resistivity logs and gamma logs that can provide data on geology, individual fractures and fluid. Other logging methods include optical and acoustic imaging methods, heat pulse flowmeters, digital borehole imaging, borehole radar and resistivity tomography.

Groundwater flow models. Numerical models are constrained in fractured-rock settings that have significant anisotropy and heterogeneity. Scientists can, however, successfully evaluate groundwater and surface water with watershed scale models. To evaluate flow in discrete fracture networks, scientists can use fracture network models; insufficient data and poor depth correlations, however, can limit model usefulness.

Reference

Wireman, M., "Characterization and Management of Ground Water Resources in Fractured-Rock Hydrogeologic Settings," *Ground Water Monitoring and Remediation*, Vol. 23, No. 3, 2003, <http://www.ngwa.org>.

See also:

- "Bioremediation in Bedrock: Using Bioremediation to Treat Dissolved BTEX and MTBE in Fractured Bedrock," D. Laughlin, *Soil, Sediment and Water*, March/April 2003; <http://www.aehsmag.com>
- "Integrated Methods for Characterizing a Fractured Rock Aquifer," <http://clu.in.org/techpubs.htm>

UTTU thanks Mike Wireman, Wireman.Mike@epamail.epa.gov, for his help on this article.



Protecting fueling systems from natural disasters

By Bill Greer, Tim Laughlin and Doug Howey

On September 16, 1999, Hurricane Floyd devastated eastern North Carolina when more than 20 inches of rain fell within a 24-hour period. Rivers, ponds and creeks were already overflowing from the downpours caused by Hurricane Dennis just 10 days earlier. Many flooded areas were beyond the 500-year floodplain. Whole towns and parts of several cities were submerged for more than a week.

The wakeup call

For those of us involved in the design, construction and operation of fueling facilities, the effects of Hurricane Floyd sounded an alarm: serious problems require immediate attention. What can be done during the design and installation stage and the day-to-day operations of a fueling facility to minimize damages in the event of a disaster such as a hurricane or flood? What should be

done in the aftermath of such an event?

Disaster preparedness—knowing what to do both before and after the disaster—can be divided into four stages:

- installation
- routine maintenance
- between the warning and the disaster (time permitting)
- post-disaster

Good installation is good preparation

The Petroleum Equipment Institute's PEI RP100, *Recommended Practices for Installation of Underground Liquid Storage Systems*, covers the subjects of supports and anchorage of USTs in "areas subject to flooding."

First, UST owners need to evaluate the site's disaster potential. Is the site subject to flooding? What if the site is where there has never been a flood, such as in many of the sites flooded by Hurricane Floyd? It is hard for UST system owners to justify an expense for something presumably extraneous. If in doubt, anchor the tanks. Remember: it is far easier to do this during installation, before adding backfill.

With respect to UST anchorage in areas subject to flooding, PEI RP100 states: "The calculation of tank buoyancy should be based on the worst case conditions, that is, water level at finished grade and the tank empty." Appendix A of PEI RP100 has instructions for calculating the weight of backfill materials and paving necessary to overcome tank buoyancy.

Another option is to use a bottom hold-down pad or deadmen anchors. Consult the tank manufacturer's installation instructions to determine what will be needed.

The latest edition of PEI RP200, *Recommended Practices for Installation of Aboveground Storage Systems for Motor Vehicle Fueling*, contains a new paragraph, Emergency Planning, which states: "In areas subject to

flooding, make provisions to prevent tanks from floating. In areas subject to hurricanes or other significant storm events, make provisions to secure tanks against anticipated wind loading. In all cases, consideration should be given to containment of releases."

Improperly anchored aboveground storage tanks were a major problem after the flood. Aboveground tanks that floated away numbered in the hundreds.

PEI RP200 gives the method of calculating the weight required to secure an AST. This is determined by multiplying the capacity of the tank (below the maximum anticipated flood stage) by the weight of water (8.3 pounds per gallon) and subtracting the weight of the tank, equipment and attached supports.

Modifications after installation

What about existing UST and AST installations? The options are few and costly for UST installations in cases in which

- no extra protection was provided for tanks subject to floating
- the anchoring conditions of the tanks are unknown

Short of excavating the tanks and reinstalling them with proper anchorage or uncovering the tanks completely and adding to the thickness of existing pavement over the tanks, nothing can be done.

AST installations, on the other hand, can be modified by adding anchoring to the tanks. Many ASTs are welded to steel saddles that can be bolted to the concrete. Others can be anchored by means of adding straps/cables and securing them to the concrete pad. As stated in PEI RP200, consult the tank manufacturer or other adequately qualified individuals. Unit tanks, which are ASTs mounted in their own steel containment dike, should also be anchored in place.

Good maintenance adds to readiness

Routine maintenance, which will take care of some obvious problems that could occur after a hurricane or flood, should include

- making sure fill caps are seated properly with O-rings/seals that are in good condition and secure; this will help keep water from entering the tanks
- ensuring that impact valves are in good condition and that trip levers work properly
- maintaining accurate inventory records to help determine how much product is lost if anything causes a release
- taking measurements of tank diameters and recording them as reference points for future measurements to determine damage

Responding to warnings

For earthquake disasters, there is no warning. For hurricanes and floods, however, there may be enough advance warning to take action without jeopardizing personal safety and protection. If time allows:

- record manual or automatic tank gauge readings of the tank before you take it out of service
- check fill caps and adapters for tightness, and make sure they are locked in place
- check any other possible openings where water could enter, including interstitial space of a double-wall tank
- if there is a ball valve or other block valve on the product piping at the submerged pump, close and secure it
- at the dispensers, close all impact/emergency valves by tripping the lever; even if your dispensers don't get submerged, the force of flood water or other floating objects could knock dispensers loose

- turn off all power to pumps and dispensers, automatic tank gauges and other components
- for USTs, the product level in the tank doesn't matter as long as the tank has adequate anchorage to prevent floating; consider filling the tanks with product if you are uncertain that your tanks are anchored; however, the risk you take is that no matter what you do, you cannot ensure the integrity of the system, and water may enter the tanks and displace product into the environment
- if there is any possibility that flood levels could reach higher than the tank vents (12 feet), extend them with PVC pipe or other means
- unit aboveground storage tanks (steel tanks mounted in their own steel containment dikes) should have the dike drainage valves opened; this will allow flood water to enter the diked areas and help keep the unit tank from moving

After the flood

After flood waters have receded, many things can and should be done to get equipment back into working condition. Laughlin and Howey developed the following lists of things to do.

General precautions:

- do not turn on any equipment until it has been examined; copper wiring in contact with water can quickly corrode; have a technician and electrician examine the condition of the equipment and AC power service and make any needed repairs before restoring power; this includes fueling systems, leak-detection equipment and corrosion prevention (impressed current) equipment
- open all electrical junction boxes, dispenser heads and pulser boxes and allow them to completely dry out before powering up; check for water in conduit; test for possible insulation damage, shorts or opens;

vacuum conduit to remove water; replace defective wires

- do not operate the submerged pump or dispenser if there is any chance that water may enter the system; pumping water will damage hydraulic components

AST-UST systems:

If flooding (e.g., surface water in excess of one foot above the ground surface) has caused tank surface settlement or heaving, excavation will be necessary to properly inspect UST system component conditions. Where movement is not obvious, the following is recommended:

- piping systems may be stressed from soil movement during periods of high water; severe movement may place stress on piping runs and lesser movement may loosen threaded connections; pipe and vent risers should be inspected to determine if they are higher, lower or more tilted than originally; if this inspection indicates movement, conduct a precision pipe tightness test; also, in double-wall piping systems, make sure all water has been excavated from the interstitial space
- tanks may be stressed due to the additional weight of water during flood conditions; standard allowable fiberglass and steel tank installation depths (i.e. distance from tank top to ground pavement surface) currently are seven and five feet, respectively; tanks at near-maximum burial depths and in high flood water may be overstressed and suffer wall failure; tank backfill stability may be affected when the surrounding soil has been disturbed by floodwater, which results in excessive tank deflection; owners should stick their tanks for the first few weeks, documenting product height and presence of water; excessive water accumulation may indicate failure of product piping, vent piping or tanks

- changes over time—in measurements of the fill adapter/tube in relation to some non-movable reference point—may indicate tank movement; tank movement, in addition to possibly damaging the tank, can cause failure of the piping connections to the tank; tank movement can also cause the tank to tilt and allow water to accumulate in the lower end
- check for tank deflection; remove the submerged pump (check electrical systems for water beforehand) and the fill-pipe drop tube; measure for deflection at these two locations as follows:
 1. drive a non-sparking nail halfway into a wooden dipstick at the one-inch mark
 2. measure and record the distance from the tank bottom to the top of the fitting
 3. pull the dipstick up until the nail catches on the inside top of the tank and measure to the top of the fitting; subtract one inch from this measurement
 4. subtract the measurement in step 2 from that in step 3 and compare to the standard tank diameter
 5. if the tank has deflected greater than two percent of the inside diameter, call the tank manufacturer for recommendations
- double-wall tanks with a brine-filled interstitial space should not be affected by water flooding since brine is heavier than water; check the brine level in the reservoir standpipe to verify that it is within the manufacturers' recommended range
- for double-wall tanks with a dry interstitial space, the probe should be removed and the interstitial space inspected for water; if present, water should be removed; however, this may prove difficult in most tanks; one option would be to convert the dry annular space to a hydrostatic system; this should only be done with the approval of the tank manufacturer and according to their instructions

- USTs that have floated out of the ground should be recertified by the tank manufacturer before reinstalling to make sure they are still suitable for service; on an STI-P3 tank, for example, the tank manufacturer will inspect the nylon bushings, anodes, exterior coating and welds; if testing the tanks with air pressure is necessary, the tanks will require cleaning and vapor freeing before adding air
- check tanks for water and sediment; if any is found, tanks should be drained, cleaned and filled with fresh product; remember: petroleum-contaminated water is a hazardous waste and must be disposed of properly; contact a licensed hazardous waste transporter to pump water out of your tanks
- a precision test of the entire UST system should be conducted before restarting
- a qualified petroleum equipment contractor should be contacted to correct any damage to petroleum storage systems

Dispensers:

- remove lower panels to expose the hydraulics section to the air; replace panels only when section is cleaned and fully dried
- dirt and silt may be washed away with clean water; air-dry the washed components before replacing
- remove cover from junction boxes; remove silt and other impurities; disconnect each wire nut connection, scrape away any corrosion from wires or cut wires before wire nuts; air-dry the junction boxes; when dry, replace covers
- remove pulsers; discard and replace
- examine the IS barriers (Intrinsically Safe) and connectors; if there is any sign of corrosion, replace covers

- remove the motor of self-contained pumps and take it to a repair shop for cleaning, drying and lubrication; wash away any dirt accumulation from the pumping unit and air-dry
- wash, clean and air-dry entire hydraulics area
- wash and wax external dispenser surfaces; use automotive cleaning and waxing preparations
- pumps and dispensers that have been completely submerged may require complete refurbishment; use a qualified petroleum equipment contractor or return the equipment to the manufacturer for refurbishment; in some cases, it may be practical to send the pump head only and restore the hydraulic section on site

Other electronic equipment:

- consoles that have been submerged should be replaced
- all tank level probes and sensors should be inspected for physical damage
- debris should be removed from all sensing elements
- sensors that have been embedded in mud or sensors that do not actuate freely should be replaced
- sensors should be actuated and alarm results noted at the console; sensors that do not operate properly should be replaced
- line leak tests should be completed and recorded for systems with electronic line leak detection

References

Greer, B., Laughlin, T. and D. Howey, "Protecting Fueling Systems from Natural Disasters," *Petroleum Equipment & Technology*, December 1999.

PEI, <http://www.pei.org>

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Guest editor's note: This article did not address the possible adverse impacts of flooding on existing leaks and/or the operation of existing remediation systems. For example, the operation of a free-product recovery system may be adversely affected due to the rising water table and/or water coming down on top of the existing sparge systems. The possibility of water rising in the vadose zone and/or flooding should be considered during initial planning/engineering stages. Also, if soil vapor extraction systems are operational in the vadose zone, they may be flooded and inoperable, and their use may be temporarily discontinued.



MTBE history, usage, sources and treatment

Fuel companies have used fuel oxygenates in gasoline for more than 20 years. Originally, oxygenates were used to replace tetra-ethyl lead. The Clean Air Act Amendments (CAAA) of 1990 mandated use of reformulated and oxygenated gasoline in certain urban regions, and use of MTBE increased significantly. "To meet the requirements of the CAAA, the United States Environmental Protection Agency (U.S. EPA) initiated

the Oxyfuel Program in 1992 and the Reformulated Gasoline Program (RFG) in 1995. The former required the use of gasoline with 2.7 percent oxygen by weight during the winter months to control carbon monoxide emissions and the latter required the use of gasoline with 2 percent oxygen throughout the year in ozone nonattainment areas. In addition, some cities elected to use the oxygenate-blended fuels to enhance air quality" (Deeb and others, 2003).

Guest editor's note: It was recognized early during the reformulation programs that the presence of MTBE, ethanol and other oxygenates in the fuels could adversely impact groundwater, directly and indirectly, in the event of a release. Directly, the oxygenates are more soluble in the water than the petroleum hydrocarbon constituents of fuels. Thus, when an oxygenate-containing fuel is released to the subsurface and comes in contact with groundwater, there is a partitioning effect that results in the transfer of the oxygenate from the fuel to the groundwater. Indirectly, fuel constituents such as BTEX may have a greater solubility in a groundwater-oxygenate mixture than in groundwater alone. The goal, however, at the time was focused on attainment of air emission requirements and removal of lead from gasoline.

There are two types of fuel oxygenates: ethers and alcohols. Ethers approved by the U.S. EPA include

- MTBE, methyl tert-butyl ether
- TAME, tert-amyl methyl ether
- DIPE, diisopropyl ether

Alcohols oxygenates include

- EtOH, ethanol
- TBA, tert-butyl alcohol
- MeOH, methanol

MTBE is the most widely used oxygenate in the United States because of its "high octane level, low cost of feedstocks (MeOH and isobutylene), low production

cost, ease of blending with gasoline and ease of transfer and distribution. In a reformulated gasoline, MTBE percentage on a volume basis can be as high as 11 to 15 percent" (U.S. EPA, 1998a in Deeb and others, 2003).

The second most widely used oxygenate is EtOH. "The EtOH fuel industry was created in 1978 in the United States with the passage of the Energy Security Act. The purpose of this act was to increase gasoline availability during the oil embargo and to decrease dependence on imported oil" (Deeb and others, 2003). TBA and MeOH are not as attractive oxygenates as EtOH because of their toxicity.

MTBE groundwater contamination problems have compelled fuel companies to search for other oxygenates; their use will depend on "chemical availability, performance characteristics, production and distribution costs, and potential environmental impact" (Deeb and others, 2003).

MTBE sources

Point sources of oxygenates include

- releases from USTs and pipelines
- spills at industrial plants and refueling facilities
- accidental spills during transport

The most serious threat to groundwater is release of oxygenated gasoline from USTs. Information on UST releases can be found in the Corrective Action Database at <http://www.epa.gov/swrust1/cat/camarchv.htm>. In 1998, there were 37,550 identified LUSTs, 22,790 of which contained MTBE. This resulted in 2,420 incidents of groundwater contamination and 790 incidents of surface water contamination.

Data on industrial releases of MTBE can be found at <http://www.epa.gov/tri>. Most of the releases were to the atmosphere. Deeb and others (2003) report that "Interestingly, there is no distinct correlation between

the mass of MTBE released and the increase in MTBE usage after the Clean Air Act Amendments of 1992."

Other point sources include releases from recreational vehicles and accidental spills during transport and fueling. Recreation vehicles impact surface waters by releasing unburned fuel into the water; two-stroke engines can release up to 30 percent of their fuel unburned. Modeling, however, suggests that most of the MTBE is volatilized. Although the U.S. Coast Guard tabulates spill data, releases are reported in broad categories and not as specific chemicals (<http://www.uscg.mil/hq/g-m/nmc/response/stats/ac.htm>).

Small spills of less than one gallon can occur during fuel handling; however, modeling again suggests that most of the MTBE would be volatilized before reaching groundwater. Releases from ruptured tanks or backyards "are expected to result in detectable concentrations of MTBE in groundwater. The impact of such releases to groundwater is strongly dependent on site hydrogeology" but expected to be minor (Deeb and others, 2003).

A study of fuels in Connecticut indicated the presence of MTBE in heating oil and diesel fuel; of the 78 confirmed releases that resulted in groundwater contamination, 73 percent of the sites exceeded federal drinking water advisory levels of 20 µg/l. The MTBE source was not identified nor is it known if MTBE in heating oil and diesel fuel is a nationwide occurrence.

Nonpoint sources of oxygenates include

- exhaust and evaporative emissions from vehicles
- stormwater runoff and atmospheric deposit

"Once in the atmosphere, MTBE is primarily removed by photochemical degradation and to a much lesser extent by precipitation (Zogorski and others, 1997 in Deeb and others, 2003). In urban settings, MTBE partitioning into precipitation can result in low but detectable

(> 1 ppb) concentrations of MTBE in surface water" (Deeb and others, 2003). One study of 592 stormwater samples indicated that 7 percent of the samples tested positive for MTBE, whereas a subsequent study suggested stormwater MTBE accumulated from atmospheric deposition.

Oxygenate occurrence

Environmental occurrences of fuel oxygenates, with the exception of MTBE, are not well documented because the Clean Air Act, Clean Water Act and Safe Drinking Water Act do not require monitoring in air, surface water, groundwater or drinking water. For instance, EtOH is not monitored because it has neither a drinking water standard nor an advisory limit. Limited occurrence data exists for ETBE, TAME and DIPE, with more for TBA because TBA occurs as an impurity in MTBE and MTBE breaks down and can be hydrolyzed to TBA.

Guest editor's note: Why shouldn't EtOH be monitored? There is a standard for its concentration in blood samples. Why shouldn't there be a standard for its concentration in water that could potentially be public drinking water sources?

Deeb and others (2003) examined MTBE detections in three states: California, Massachusetts and Maryland.

California. California's drinking water standards "for MTBE are 13 µg/l (primary health-based standard) and 5 µg/l (secondary standard, based on taste and odor concerns)" (Deeb and others, 2003). Data show that MTBE surface and groundwater detections increased until 1999 and, after that, leveled off or decreased. This may result from watershed protection measures that prohibited two-stroke engines on many reservoirs. Sampling patterns may also affect the data.

Massachusetts. Massachusetts' drinking water guideline for MTBE is 70 µg/l. The secondary standard is 20 to 40 µg/l, and required detection limit is 5 µg/l. Massa-

chusetts began compiling data in 1993, but monitoring was not required until July 1999. Data from 2000 to 2001 indicated that 1 to 2 percent of sampled public water supplies had detectable MTBE.

Maryland. Maryland began voluntary sampling for MTBE in January 1995 at an action level of 20 µg/l. "Since 1995, MTBE was detected in approximately 100 of the 1,200 public water systems sampled. Thirteen systems had detections greater than 20 µg/l and were taken out of service or had levels that dropped below 20 µg/l. Surface water impacts were negligible" (Deeb and others, 2003).

Although MTBE data in these three states are not necessarily representative of states nationwide, "The data indicate that MTBE detections in drinking water supplies are likely stabilizing in frequency since 1999..." (Deeb and others, 2003).

Occurrence of MTBE with other oxygenates

Researchers also note that in the Charnock field (West Los Angeles), where MTBE contamination is well known, TBA (22 percent of samples) was found at a maximum value of 3,400 µg/l, whereas TAME, DIPE and ETBE were detected in less than 2.5 percent of samples and never exceeded 25 µg/l. Another study in the Los Angeles area found TBA in 33 percent of samples, TAME in 8 percent, DIPE in 14 percent and ETBE in 2 percent with mean MTBE and TBA concentrations of 7,100 µg/l and above 100,000 µg/l, respectively.

Summary of MTBE treatment technologies

Selection of an MTBE remedial technology will depend on

- volume of contaminated soil and groundwater
- contaminant concentration and mass

- site-specific hydrogeological characteristics
- risk-based or regulatory-driven cleanup objectives

Deeb and others (2003) add, "As with any remedial effort, source removal is critical for the success of remediation systems at MTBE-impacted sites. Due to the hydrophilic nature of MTBE, rapid responses to releases of MTBE-containing gasoline are essential to minimize site characterization and remediation costs."

Techniques that have successfully treated MTBE-contaminated sites include

- soil vapor extraction
- multiphase high-vacuum extraction
- conventional pump-and-treat along with air stripping and granular activated carbon

The presence of TBA complicates matters because TBA's high polarity means that it sorbs only weakly onto activated carbon, rendering air stripping technologies ineffective. The combination of biodegradation and granular activated carbon, however, is effective, as is advanced oxidation with reverse osmosis.

Emerging technologies with promise include

- chemical oxidation
- bioremediation/bioaugmentation
- phytoremediation
- sorption on synthetic resins
- advanced oxidation processes
- biological treatment

A promising technique, not yet tested at the field level, uses membranes or solvent extraction for MTBE removal from water.

As for natural attenuation, studies have shown that aromatics in gasoline slow biodegradation rate. Conditions favorable to natural attenuation of MTBE include an enhanced indigenous microbial population with

prior MTBE exposure, presence of electron acceptors and nutrients, and favorable pH. According to Deeb and others (2003), "Considering the observed persistence of MTBE in subsurface environments around the country, it is unlikely that natural attenuation would be an acceptable sole remedy at most MTBE-impacted sites...significant biodegradation of MTBE in aquifers has not been commonly observed. Thus, it is important not to extrapolate laboratory MTBE degradation rates to the field, especially when estimating whether degradation will be rapid enough to sustain significant plume shrinkage over time."

See also the UTTU Web site (<http://uttu.engr.wisc.edu>) for other articles on MTBE remediation.

Research needs

Deeb and others assert that "Perhaps one of the most important emerging issues related to oxygenates is the validity of the analytical data generated to date. Even though early problems and uncertainties associated with analytical methods have been largely overcome, the extent of ether hydrolysis to alcohols following the preservation of groundwater samples with acid remains unknown... As a consequence, ether concentration (e.g., MTBE) in groundwater samples may be underestimated while alcohol concentration (e.g., TBA) may be overestimated."

Research needs include the following:

- technologies to effectively remove TBA
- biological approaches at oxygenate-contaminated sites
- bioaugmentation of MTBE, when oxygen or other nutrient supplements are necessary
- anaerobic biodegradation of MTBE and TBA
- effective oxygen delivery at highly reducing sites

- application of natural attenuation of MTBE and TBA as a stand-alone strategy
- impacts of EtOH on the environment
- improved methods to prevent future gasoline releases

Reference

Deeb, R.A., Chu, Kung-Hui, Shih, T., Linder, S., Suffet, I., Kavanaugh, M.C., and L. Alvarez-Cohen, "MTBE and Other Oxygenates: Environmental Sources, Analysis, Occurrence and Treatment," *Environmental Engineering Science*, Vol. 20, No. 5, 2003; <http://www.liebertpub.com/EES>



Research Notes

Aggregate soil size in transport and reaction processes in bioremediation

Loftabad, S.K. and M.R. Gray, *International Journal of Chemical Reactor Engineering*, Vol. 1, Article A 19, 2003; <http://www.bepress.com/ijcre/vol1/A19>

Loftabad and Gray (2003) designed experiments "to determine the effect of aggregate size and NAPL distribution within the soil matrix on the rate of bioremediation and to evaluate how the extent of bioremediation is affected by aggregate size in the range 40 to 1,000 microns in a mixed-reaction environment." Soils were tested in an active mixed culture in slurry bioreactors, and some samples were sonicated.

"Bacterial degradation of two-, three- and four-ring compounds is widespread, but degradation of higher-molecular-weight compounds is more difficult, possibly due to a combination of low flux and more difficult conversion to useful cellular intermediates. The low aqueous solubility of PAHs (polycyclic aromatic hydrocarbons) ensures

low mobility, so that biodegradation must almost always focus on conversion of PAHs found in a soil matrix. The distribution of compounds in the soil, and their rate of release to the aqueous phase, often controls biodegradation rate" (Loftabad and Gray, 2003).

Non-biological processes often dominate PAH and other low-solubility compound biodegradation. Important kinetic processes include

- interphase transport, which is a function of the interfacial area and contaminant concentration in the NAPL phase
- processes associated with interfacial barriers between the NAPL and aqueous phase, which can include biofilms and chemical films at interfaces
- partitioning and kinetic processes in desorption from soil organic matter
- processes associated with internal diffusion of contaminant through soil aggregates
- diffusion through the aqueous phase from soil aggregates to microorganisms

Other studies have shown that "the NAPL in aged soils occurred as thin domains bounded by clays, and that the NAPL served as a binder within the soil matrix. In this case, the diffusion of contaminants through tortuous paths in soil aggregates could account for some of the slow release of PAH from long-term contaminated soils" (Loftabad and Gray, 2003).

These scientists used mixed-slurry-phase reactors to overcome mass transfer limitations. "Mixing provides a uniform distribution of nutrients, oxygen and contaminants, as well as increasing the interfacial areas of the NAPL with the aqueous phase. Slurry-phase bioreactors eliminate the resistance to mass transfer from soil aggregates to the microbes."

Loftabad and Gray (2003) concluded the following:

- the PAHs show a preferred sequence of biodegradation, which appears to be related to molecular structure and complexity: microorganisms preferentially degraded the simpler molecules
- because of strong adsorption to soil organic material, rates of release from NAPL-filled pores are slow
- "sonication of the soil to disperse soil aggregates increased the rate of microbial degradation up to 5-fold; however, there was no significant difference in the final residual concentrations between the two soil treatments"
- after an initial lag period, rapid degradation started in both sonicated and non-sonicated soils
- the effect of sonication was more significant for the higher-molecular-weight compounds
- in the bioreactor, hydration and shear forces changed soil aggregate size and distribution

Backward location and travel time probabilities for a decaying contaminant in an aquifer

Neupauer, R.M. and J.L. Wilson, *Journal of Contaminant Hydrology*, Vol. 66, 2003; <http://www.elsevier.com/>

Scientists developed one-dimensional models "to verify higher-dimensional numerical models of backward location and travel time probabilities." These analyses can be used to "determine the prior position of contamination in an aquifer... Backward modeling produces location and travel time distributions. Backward location probability describes the likely position of the detected contaminant particle at some time in the past, and is related to resident concentration. Backward travel time probability describes the time prior to detection that the

detected contaminant particle was at an upgradient location, and is related to flux concentration."

Nitrate-consuming processes in a petroleum-contaminated aquifer quantified using push-pull tests combined with ¹⁵N isotope and acetylene-inhibition methods

Schurmann, A., Schroth, M.H., Saurer, M., Bernasconi, S.M. and J. Zeyer, *Journal of Contaminant Hydrology*, Vol. 66, <http://www.elsevier.com/>

Scientists recently completed three push-pull tests (PPTs) in a heating-oil contaminated aquifer that had been injected with a tracer (Br) and ¹⁵N-labeled NO₃⁻. NO₃⁻ had been injected in other petroleum-contaminated aquifers to stimulate and enhance denitrification. Scientists obtained quantitative information on in-situ microbial activities in order to understand microbial processes and predict degradation rates.

Schurmann and others (2003) used single-well PPTs to "determine accurate and reproducible rate coefficients of NO₃⁻ consumption in-situ in a PHC-contaminated aquifer. The combination of PPTs, ¹⁵N-isotope and C₂H₂ inhibition methods provided improved information on denitrification as well as alternative fates of NO₃⁻... In particular, we demonstrated that rate coefficients of NO₃⁻ consumption during a test may significantly overestimate denitrification activity. Using ¹⁵N-isotope and C₂H₂ inhibition methods in combination provided indication for abiotic NO₃⁻ (or NO₂⁻) reduction in this aquifer, although a precise quantification of this process may require additional tests."

Protocols to enhance biodegradation of hydrocarbon contaminants in soil

Gray, M.R., Banerjee, D.K., Dudas, M.J. and M.A. Pickard, murray.gray@ualberta.ca

Researchers designed experiments to determine when microbial metabolism limits contaminant removal from soil. Creosote- and diesel-fuel-contaminated soils were used.

Protocols tested to enhance hydrocarbon removal include

- stimulation of bacterial cultures with either naphthalene or a mixture of anthracene and phenanthrene; the lower-ring PAH, as a more easily metabolized energy source, would presumably induce enzyme activity
- use of static conditions to enhance bacterial attachment to the non-aqueous phase liquids in the soil; this would "promote direct attachment of bacteria to the remaining NAPL...and encourage further degradation despite low aqueous phase concentrations
- increased incubation temperature

Results suggest that "desorption of contaminants from the soils limited the ultimate removal of contaminants, not the biological activity."



Information sources

U.S. EPA publications and information

National Institute for Environmental Health Studies (NIEHS) *Biosensors for Environmental Monitoring*, a new Internet seminar, is available at <http://www.clu-in.org/studio>.

"Sampling for Contaminants in Sediments and Sediment Pore Water" can be viewed at <http://clu-in.org/programs/21m2/sediment/>

Technology News and Trends, which can be downloaded from <http://clu-in.org/techpubs.htm>, contains articles on steam injection and electrical resistance heating, biological permeable reactive barriers, and integrated methods for characterizing a fractured-rock aquifer.

Other documents and Web sites

- *Groundwater Remediation Strategies Tool*, (Publication No. 4730) is available from API, American Petroleum Institute, <http://api-ec.api.org/>
- *ITRC Quarterly Update*, <http://www.itrcweb.org/ITRC0903Update.pdf>, contains publications on diffusion samplers (February 2004), sampling, characterization and monitoring of brownfields, phytotechnologies and in-situ bioremediation
- *Light Non-Aqueous Phase Liquid (LNAPL) Parameters Database* (Publication No. 4731), is available from API, <http://groundwater.api.org/lnapldatabase/>
- *MTBE Remediation Handbook*, by Ellen Moyer and Paul Kosteki, April 2004, was recently published by Kluwer Academic Publishers and is available for \$120; call 781-871-6600 or e-mail kluwer@wkap.com

- *Site Assessment and Remediation Handbook*, 2nd Ed., by Martin N. Saram, 2003, is available from Lewis Publishers, <http://www.crcpress.com>, for \$159.95.

UTTU obtained many of these sites from TechDirect (<http://www.clu-in.com/techdrct>), Ground Water Monitoring & Remediation (<http://www.ngwa.org>), and other publications. We thank the editors and writers for allowing us to reprint this material.