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Degradation of BTEX and MTBE in an MTBE-degrading culture

Deeb and others (2001) investigated substrate interactions that occur during the aerobic biotransformations with PM1, a pure culture that uses MTBE for growth. Although several laboratory studies have demonstrated MTBE's biodegradability, there is "no convincing evidence to date that MTBE biodegradation occurs rapidly in the field under natural conditions." Researchers wanted to determine if

- the presence of MTBE negatively impacts BTEX attenuation, leading to BTEX plume elongation
- ease of BTEX degradability causes repression of MTBE degradation

Researchers used a pure culture capable of utilizing MTBE for growth. "Pure cultures can be useful for characterizing the nature of inhibition or stimulation of a phenomenon observed during the biodegradation of contaminant mixtures" (Deeb and others, 2001). In addition they studied MTBE and BTEX biodegradability with various substrates: MTBE alone, or MTBE in substrate mixtures with each of the BTEX compounds.

Culture PM1

Attributes of PM1 include the following:

- member of the *Leptothrix* branch of *b-Proteobacteria* (a bacterial strain)
- capable of degrading MTBE to CO₂
- can effectively utilize TBA (tert-butyl alcohol)

Researchers isolated the bacterial strain PM1 from an MTBE-degrading mixed culture obtained from a compost biofilter at the Los Angeles County Joint Water Pollution Plant in Carson City, California.

Procedure

Researchers grew the culture in 250-ml bottles using a mineral salts medium and either MTBE or BTEX as the carbon and energy source. MTBE was added at concentrations of 20 to 100 mg/L. An increase in turbidity in the bottles indicated growth had occurred, and MTBE concentration was increased to 500 mg/L. After approximately four days, MTBE was degraded and cells were harvested, resuspended, and then used in biotransformation experiments.

PM1 was grown on benzene using initial benzene concentrations of 40 mg/L. When the benzene was depleted, benzene, at concentrations of 40 mg/L, and oxygen were added to bottles. Following cell inoculation, MTBE and BTEX concentrations were monitored using gas chromatographs (GC) equipped with either flame ionization (FID) or photoionization detectors (PID).

Results

Results from studies indicated the following for pure MTBE-grown cells of PM1:

- PM1 biodegraded both MTBE and benzene at rates of 5.0 and 1.1 mg/L, respectively
- MTBE degradation commenced without a lag
- benzene did experience a lag of about 20 hours, presumably due to induction of enzymes for benzene degradation, possibly suggesting different degradation pathways for BTEX and MTBE
- once cells were induced for benzene, sequential additions of benzene or toluene were degraded without a lag

In an MTBE mixture, researchers found

- the lag phase for benzene was 4 hours and degradation rate was 5.5 mg/L/hr (suggesting MTBE presence enhances benzene degradation, or energy generated during MTBE degradation allows for efficient production of enzymes needed for benzene degradation)
- a 3-phase pattern for MTBE:
 - MTBE degradation proceeded initially at a fast rate without a lag period
 - once benzene degradation accelerated to significant levels (3-7.5 hours), MTBE degradation rate slowed significantly
 - MTBE degradation rate increased only when benzene was nearly gone

Next, to evaluate benzene degradation in the presence of MTBE, researchers took MTBE-grown PM1 cells and exposed them to benzene in mixtures with either MTBE, a rich carbon source such as pyruvate, or ethanol. In these mixtures, at 20 mg/L concentrations:

- benzene degradation showed shorter lag periods and more rapid degradation rates than when only benzene was present
- benzene degradation rate with increased pyruvate (50 and 100 mg/L) concentrations showed no increase over the previously added 20 mg/L concentrations of pyruvate, ethanol or MTBE

- pyruvate and ethanol presence had little effect on MTBE degradation in MTBE mixtures
- benzene presence retarded MTBE degradation
- when additional benzene was added, it was degraded, without a lag period, at higher rates than listed above

With benzene-grown cells of PM 1:

- benzene, toluene and ethylbenzene were rapidly degraded without a lag period
- MTBE was slowly degraded following a lag of more than 10 hours

Next, researchers used other substrates (such as toluene, ethylbenzene, and *m*-xylene and *p*-xylene) to evaluate the longevity and nature of benzene- and MTBE-induced activities. Trends were similar to those reported with benzene/MTBE mixtures; however, MTBE-grown cells of PM 1 could not degrade toluene in the absence of MTBE. This effect is more pronounced at low culture inoculum densities. Degradation of ethylbenzene was also evaluated at various ethylbenzene concentrations in MTBE-grown cells of PM 1.

Conclusions

Researchers concluded the following from these experiments:

- these studies suggest that BTEX compounds are responsible for the inhibition of MTBE degradation
- the presence of MTBE in mixtures with BTEX compounds does not appear to inhibit BTEX biodegradation in the MTBE-degrading culture PM 1
- the presence of MTBE in MTBE-grown cells actually stimulates BTEX biodegradation
- MTBE appears to promote benzene degradation by generating energy that accelerates the induction of the enzymes of the benzene degradation pathway (pyruvate and ethanol had the same enhancement effect on benzene degradation as MTBE, suggesting that the carbon source was not the factor that governed the enhanced induction of the benzene pathway; rather, an "energy generator" was the critical factor)
- the MTBE pathway might be a minor pathway for benzene degradation before the principal pathway for benzene degradation is induced, or low levels of benzene might be degraded constitutively by PM 1 (researchers suggest the latter scenario is more likely)
- benzene and MTBE pathways remain active for longer periods in the absence of an inducer when an energy-supporting substrate is provided

- ethylbenzene and xylenes severely inhibit MTBE degradation by PM 1
- toluene and benzene are preferentially utilized over MTBE in mixtures following inductions of an aromatic degradation pathway
- if subsurface microorganisms behave similarly to PM 1, then bioattenuation of MTBE could be inhibited until the MTBE migrates beyond the BTEX components in the plume
- by depleting oxygen, alternative electron acceptors or nutrients during degradation, BTEX compounds could suppress MTBE degradation
- the presence of alternative growth-supporting substrates, such as pyruvate, ethanol and low concentrations of BTEX components that do not cause toxicity, could help cultures such as PM 1 to retain MTBE induction during intermittent MTBE exposure

Deeb and others (2001) believe that "most of the cultures reported to degrade MTBE have little in common phylogenetically. Studies are needed to compare the degradation behavior of laboratory-grown cultures to subsurface microbial communities to better extrapolate laboratory observations to the field."

Reference

Deeb, R.A., Hu, H.Y., Hanson, J.R., Scow, K.M. and L. Alvarez-Cohen, "Substrate Interactions in BTEX and MTBE Mixtures by an MTBE-Degrading Isolate," *Environmental Science & Technology*, Vol. 35, No. 2, 2001; <http://www.pubs.acs.org>.

UTTU thanks Dr. Lisa Alvarez-Cohen, Department of Civil Engineering, University of California, for her help on this article.



MTBE degradation in sediments

Bradley and others (2001) collected stream and lakebed sediment from 11 sites in the United States. With these samples, they evaluated MTBE biodegradation and mineralization by indigenous microorganisms using radiolabeled ^{14}C -MTBE in the lab.

The sites

Researchers chose field sites that covered a wide range in sediment geochemistry, contaminant exposure and geographical location. Thus, six sites were on the East Coast, two on the Florida Gulf Coast, one in western Texas, one in Idaho, and one in Montana. Approximately half of the sites had a history of MTBE contamination.

Microcosms

Sediment microcosms were amended with uniformly labeled $[\text{U-}^{14}\text{C}]$ MTBE. Researchers amended "20 ml serum vials with 10 ml of saturated bed sediment, sealed them with Teflon-lined butyl rubber stoppers and flushed them with 1000 ml of zero air. Triplicate experimental treatments were prepared for each sediment... Sediment microcosms were amended with approximately 0.3 μCi of $[\text{U-}^{14}\text{C}]$ MTBE. Headspace concentrations of CH_4 , $^{14}\text{CH}_4$, CO_2 , $^{14}\text{CO}_2$, and MTBE were monitored by analyzing 0.5 ml of headspace" using gas chromatography with radiometric and thermal conductivity detection. Researchers estimated the total number of microorganisms present by acridine orange direct counts.

Results

After 50 days, microcosms from each site were examined for $^{14}\text{CO}_2$ production. Samples from all sites showed significant aerobic mineralization of $[\text{U-}^{14}\text{C}]$ MTBE to $^{14}\text{CO}_2$. $^{14}\text{CO}_2$ recoveries ranged from a minimum of 15 percent (Liddy Hot Springs, Idaho site) to 66 ± 21 percent (Pensacola, Florida site). Researchers found that the loss of $[\text{U-}^{14}\text{C}]$ MTBE was not statistically significant in the sterile controls; thus, they attributed all loss to biological activity. *(Reviewer's comments: these results do not necessarily apply to groundwater systems; furthermore, the extent to which laboratory redox conditions mimic actual field redox conditions is not well known.)*

Conclusions

Bradley and others (2001) concluded the following:

- MTBE mineralization was not limited to sediments with a history of MTBE contamination
 - five sites in this study had significant MTBE contamination at the time of sample collection
 - one site had periodic exposure to low concentrations of MTBE
 - four sites had no history of MTBE contamination but a history of chlorinated solvent contamination
 - one site used pristine sediments (Liddy Hot Springs, Idaho)
- MTBE-degrading microorganisms do not require previous exposure to effectively degrade MTBE
- rapid MTBE mineralization in Pensacola Bay sediments suggests that microbial MTBE mineralization can be significant in estuarine and coastal environments as well as in freshwater systems
- the magnitude of MTBE mineralization **was not** related to number of microorganisms present in sediment samples
- the magnitude of MTBE mineralization **was** related to grain size distribution; a strong positive relationship was observed between final $^{14}\text{CO}_2$ recovery and percentage content of sand-sized grains (grain diameter between 0.125 and 2.0 mm); this is attributed to the dependence of microbial MTBE mineralization on aerobic conditions: higher sediment permeability can increase oxygen diffusion into sediments; the observed correlation between MTBE biodegradation efficiency and sediment type "may be more pronounced in-situ, where advection can transport oxygen deep into permeable sediments"; in impermeable sediments, oxygen supply is generally limited by diffusion to the upper few millimeters
- aerobic microbial degradation of MTBE may contribute to the reported transience of MTBE in surface water

Another microcosm study by Bradley, Chapelle and Landmeyer (2001) indicated biodegradation of MTBE to CO_2 under denitrifying (anaerobic) conditions and without accumulation of t-butyl alcohol (TBA).

Reference

Bradley, P.M., Chapelle, F.H. and J.E. Landmeyer, "Methyl t-Butyl Ether Mineralization in Surface-Water Sediment Microcosms under Denitrifying Conditions," *Applied and Environmental Microbiology*, Vol. 67, No. 4, April 2001; <http://aem.asm.org>.

Bradley, P.M., Landmeyer, J.E. and F.H. Chapelle, "Wide-spread Potential for Microbial MTBE Degradation in Surface-Water Sediments," *Environmental Science and Technology*, Vol. 35, 2001; <http://www.pubs.acs.org>.

See also Environmental News, "Potential Aerobic MTBE Biodegradation" in *Environmental Science and Technology*, Vol. 35, March 1, 2001; <http://www.pubs.acs.org>.

UTTU thanks Dr. Paul Bradley, U.S. Geological Survey, for his help on this article.



Field and laboratory study of MTBE phytoremediation

Hong and others (2001) recently evaluated the effectiveness of hybrid poplar trees for hydraulically containing and remediating an MTBE groundwater plume. They performed a field study in Houston; in addition, they examined the fate of ¹⁴C-radiolabeled MTBE in a laboratory bioreactor study.

Bioreactor study

Researchers used hybrid poplar cuttings in a hydroponic solution to study uptake of ¹⁴C-radiolabeled MTBE. Cuttings were eight inches long with diameters of 0.75 to 1.0 inch. "The cuttings were affixed with predrilled screw caps and predrilled Teflon-lined septa. Teflon tape was wrapped around the stem, and acrylic caulk was used to seal the caps and septa to the cutting. Poplar cuttings were rooted first in hydroponic solution until a vascular root system appeared and then placed in 1-L bioreactors containing 400 ml of nutrient solution. The bioreactors consisted of 1-L Erlenmeyer flasks modified by attaching a sampling port to the bottom and top of each flask" (Hong and others, 2001).

Researchers

- kept the trees in a laboratory growth chamber at 28°C under artificial growth lights
- used controls in the bioreactor to quantify losses from the system
- treated the bioreactor with a mixture of cold MTBE (4.32 mg) and 7.07 μ Ci of [¹⁴C]-MTBE; previous studies indicated that MTBE concentrations of less than 1,000 mg/L caused little or no toxicity to plants

- collected samples daily
- weighed bioreactors daily to gravimetrically monitor transpiration and nutrient solution

Researchers terminated the experiment after 10 days. Cuttings were bio-oxidized and counted on a liquid scintillation counter. MTBE mass balance of the bioreactor was estimated as follows:

- percent remaining in solution was 35.65
- leaks accounted for 26.85 percent
- 16.81 percent transpired from leaves
- 11.31 percent moved through the stem
- headspace removal was 5.90 percent
- 1.27 percent was removed by sampling
- bottom stems accounted for a 1.27-percent loss
- top stems contained 0.48 percent
- petioles (leafstalk, connects the blade with the stem) contained 0.21 percent
- roots contained 0.15 percent
- leaves contained 0.10 percent

Researchers pointed out that movement of MTBE through the excised stem (11.3 percent) showed that MTBE can be removed from the root zone through dead or dormant trees. In this scenario, a large fraction of MTBE would be emitted to the atmosphere; however, MTBE half-life in the atmosphere is approximately 4 days, versus a half-life of several years in groundwater. Total mass of MTBE evapotranspired from a groundwater plume by phytoremediation would be small relative to evaporative losses at the gas pump. Hong and others (2001) also report that "transport of hydrophilic compounds in the transpiration stream is generally thought to be limited due to lipid bilayers of plant membranes." Yet, "Low-molecular hydrophilic compounds such as MTBE and other oxygenates may transport through plant membranes via hydrogen bonding with water or by rendering plant membranes more permeable."

Field site

The field site in Houston, Texas, has a water table height of approximately 10 feet below grade. Other characteristics of the site included

- average groundwater flow gradient of 0.003 ft/ft
- saturated zone composed of permeable silty sand, with hydraulic conductivity of 10^{-4} to 10^{-3} cm/s
- unsaturated zone
- rainfall of about 100 cm/yr
- potential evaporative demand about 150 cm/yr

With a groundwater table of 10 feet below grade, the practical limit with respect to poplar root penetration and capillary zone uptake is very close; if the groundwater table were much deeper, phytoremediation using poplars might not be viable at this site.

Modeling, poplar planting and field study

Researchers modeled the plume and poplar action and considered time-varying root water and contaminant uptake, surface evaporation and infiltration. Their model was used to estimate actual transpiration as a fraction of potential transpiration and to estimate where trees should be planted. Thus, workers planted hybrid poplar trees in February 1998, using a defined areal coverage and geometric pattern suggested by modeling. Trees were "planted with 6 ft centers spaced 8 ft between staggered rows to maximize the rate of canopy development. The hybrid poplars were planted in deep-drilled 1 ft-diameter holes that penetrated the clay to the sandy aquifer material. Poplar whips were planted 6-9 ft below ground surface with 0.5-1 ft of whip exposed above ground" (Hong and others, 2001).

Workers are continuing to take field measurements to

- assess and fine-tune model predictions
- demonstrate phytohydraulic capture
- explore the full-scale fate of MTBE

Field measurements include vadose zone moisture profiling, direct transpiration rate measurements, leaf area measurements, analysis of root distributions, groundwater elevation and plume monitoring. Some wells have continuously logging pressure transducers, which give information on short-term events such as heavy rainfalls.

Further modeling indicated that the poplar trees could establish a well-developed canopy and root system and cause significant drawdown of the water table and create a cone of depression. Incorporated in this modeling study were transient conditions, site-specific meteorology, unsaturated and saturated zone soil characteristics/flow, infiltration and evapotranspiration and root distribution.

Conclusions

Hong and others (2001) conclude that "the hydraulic containment and remediation of MTBE by plant uptake in groundwater by deep-rooted trees appears to be a promising remediation alternative. The results of the laboratory and modeling studies as well as the preliminary results from the field study demonstrate that MTBE can be taken up by poplars (MTBE removal of 36.5-67.0 percent

within 10 days from the 400-ml reactors) and that phytohydraulic containment of an MTBE groundwater plume can be achieved. The several-year field study is intended to provide quantitative information to help support more widespread application of phytoremediation methods to various locations where there is shallow groundwater contamination."

Reference

Hong, M.S., Farmayan, W.F., Dortch, I.J., Chaing, H.Y., McMillan, S.K. and J.L. Schnoor, "Phytoremediation of MTBE from a Groundwater Plume," *Environmental Science & Technology*, Vol. 35, No. 6, 2001; <http://www.pubs.acs.org>.

See also "Transport of Methyl tert-Butyl Ether through Alfalfa Plants," by Zhang, Q., Davis, L.C. and L.E. Erickson, *Environmental Science & Technology*, Vol. 35, No. 4, 2001; <http://www.pubs.acs.org>.



Ethanol-blended gasoline benefits and concerns

Because of MTBE's possible carcinogenic effects and unfavorable aesthetic impact on drinking water quality, several states, including California, have banned MTBE and are replacing the oxygenate with ethanol. Many Midwestern states already use ethanol; for instance, approximately 95 percent of gasoline sold in the Chicago area contains ethanol (Powers and others, 2001). Ethanol can be blended with gasoline to form E10 (10 percent ethanol and 90 percent gasoline) or used in higher concentrations, such as E85 or pure ethanol (AFDC, April 2001).

Ethanol's properties

Ethanol, also known as ethyl alcohol, grain alcohol, or EtOH, has a chemical formula of $\text{CH}_3\text{CH}_2\text{OH}$. Ethanol can be considered an ethane with a hydrogen molecule replaced by a hydroxyl group. Because of the ethanol molecule's polarity, it will preferentially partition into water and has essentially infinite solubility (AFDC, 2001). Table 1 lists some common characteristics of ethanol.

Chemical formula	CH ₃ CH ₂ OH
Molecular weight	46.07
Weight of 1 gallon	6.59 lbs (100 percent/ 200 proof); 6.80 lbs (95 percent /190 proof)
Density (g/cm ³)	.791 (100 percent); .815 (95 percent)
Surface tension in dynes/cm ²	21.4@40°C
Freezing point	-117.3°C/-178.6°F
Boiling point	78.3°C

Table 1. Ethanol's common properties (adapted from ACE, 2001).

Advantages of ethanol include

- biodegradability: ethanol will biodegrade quickly in groundwater
- renewability: ethanol is made from biomass (corn, grains, potatoes)
- absence of severe health effects when dissolved in groundwater
- air pollution reduction
- no increase in carbon dioxide: the carbon dioxide released during combustion is balanced by that amount used by plants grown to produce ethanol; in contrast, incomplete burning of hydrocarbon fuels adds to the total amount of carbon dioxide existing, thereby contributing to global warming; one oxygenated diesel gasoline can cut particle emissions by 41 percent and decrease NO_x by 5 percent (*Environmental News, 2001*)

Issues of ethanol concern are described in the following sections:

- cosolvency
- sorption
- biodegradation

Cosolvency

Ethanol at all concentrations is completely miscible in both gasoline and water. "With a sufficiently large amount of ethanol in a localized subsurface environment, gasoline and water become completely miscible with each other and merge into a single phase. Although this might occur following a spill of neat ethanol into petroleum-contaminated soil at a terminal, ethanol concentrations (< 15 percent by volume in the aqueous phase) in groundwater near the site of an RFG spill are expected to be much lower than the 80 percent by volume concentrations in the aqueous phase that is required to create a single phase" (*Powers and others, 2001*).

"Aqueous-phase concentrations of ethanol that leach from an RFG or oxyfuel spill could also be high enough to increase the groundwater concentrations of individual chemical species equilibrated with the gasoline." Of concern is benzene, although "ethanol also affects equilibrium partitioning relationships by the 'cosolvent effect' which is observed as a reduction of the aqueous-phase polarity when high concentrations of polar organic compounds are present" (*Powers and others, 2001*).

Equilibrium batch experiments performed by researchers have shown an approximate logarithmic increase in benzene, toluene, ethylbenzene and xylene concentrations with increasing ethanol concentrations. Over an ethanol volume fraction of ≤ 15 percent, benzene, toluene and xylene increased from 20 to 60 percent. According to researchers, "The smallest percentage increase was observed for benzene, the least hydrophobic of the BTEX compounds. More hydrophobic compounds in gasoline, such as xylene, will have a greater percentage increase in their aqueous-phase concentrations in the presence of ethanol. These results suggest that it is unlikely that cosolvent-related increases in BTEX concentrations will be significant relative to other processes that affect field-scale concentrations following a spill of ethanol-blended gasoline" (*Powers and others, 2001*). A spill of neat ethanol at a bulk terminal could lead to an increase in BTEX concentrations of an order of magnitude.

Sorption

Ethanol presence in groundwater reduces the extent of sorption of hydrophobic compounds due to reduced polarity of the aqueous phase. Studies indicate, however, that the cosolvency effect is less significant for sorption than solubilization; hence ethanol, at the low concentrations envisioned, would have little influence on BTEX retardation.

Biodegradation

Ethanol is preferentially degraded over other gasoline constituents in both aerobic and anaerobic environments. Large concentrations of ethanol, > 100,000 mg/L, are not biodegradable and can be toxic to more organisms. Table 2 shows ethanol's half-life as influenced by electron acceptors. In addition, environmental conditions that will influence ethanol's half-life include lower microbial concentration, colder temperatures, and depletion of electron acceptors.

Electron acceptor	Half-life (days)
O ₂	2-3
NO ₃ ⁻	1-3
Fe ³⁺	4
SO ₄ ⁻²	7
CO ₂	6

Table 2. Estimated ethanol half-life (Powers and others, 2001).

In addition, ethanol has a high oxygen demand and therefore is likely to be degraded under non-aerobic conditions. Although no byproducts are toxic, there can be adverse aesthetic impacts, and high enough accumulations of acetate and other volatile fatty acids could lower pH and inhibit microbial activity.

Presence of ethanol: impact on BTEX biodegradation

Ethanol can affect BTEX biodegradation in the following ways:

- by depleting dissolved oxygen
- by depleting electron acceptors and nutrients

Modeling studies

Various modeling studies suggest that "benzene will indeed travel farthest from the site of an ethanol-blended gasoline spill. Predictions generally show that these benzene plumes range from 20 to 150 percent longer as compared with nonoxygenated gasoline. Variability in predicted plume lengths depends on the modeling study assumptions and the nature of the aquifer and transport properties involved" (Powers and others, 2001).

Monte Carlo simulations showed that "relative to risks associated with standard formulation gasoline, there is an increase in the risk that wells will be contaminated by RFG using either MTBE or ethanol as an oxygenate. With ethanol, the risk of contaminating wells decreases after approximately five years" (Powers and others, 2001). This is not the case with MTBE, which shows recalcitrance to biodegradation.

Conclusions and direction of future work

Powers and others (2001) conclude that "although modeling studies show that assumed biodegradation rates have a significant impact on the predicted increase in benzene plume lengths, currently available research results quantifying these rates are limited in number and scope." It would be helpful to researchers to have more information on how substrate interactions affect degradation kinetics.

Additional areas requiring future study (experimental, modeling, field studies) include:

- rates of ethanol partitioning from a gasoline spill to groundwater
- nature of gasoline pools when ethanol is present or spilled into an existing pool

Researchers also indicate that a lack of a historical database and databases that do not differentiate among gasoline types confound efforts to understand ethanol impact in the field. They recommend monitoring for ethanol and aquifer redox state in an effort to determine ethanol impact on groundwater.

Economics of ethanol

Ethanol producers are testing new feedstocks and production technologies in an effort to bring down the cost of ethanol production (Deutsch, 2000). Because feedstocks can account for up to two-thirds of production costs, ethanol sources other than corn can include

- agricultural wastes, such as rice straw and sugar cane waste
- forestry residues
- municipal solid wastes
- other low-value biomass, such as sweet potatoes

In the United States, ethanol plants in the developmental stage are projected to produce 318 million gal/year of ethanol. 1998 cost data for ethanol and wholesale gas production indicated the following:

- ethanol produced from cellulose: \$1.15 to \$1.43/gal
- ethanol produced from corn: \$1.10/gal
- wholesale gasoline: \$0.80 to \$0.90/gal

Clearly, ethanol produced from cellulose can cost significantly more than ethanol produced from corn or gasoline without ethanol. By 2015, however, ethanol production costs from cellulose are expected to plummet to \$0.69/gal.

New technologies of ethanol production being considered include enzymatic conversion of biomass, biotech-based processing to produce ascorbic acid from glucose, acid hydrolysis (dilute, concentrated, countercurrent), and use of microbes capable of fermenting the full range of sugars found in biomass.

Another study by Pimentel (Troughton, 2001) indicated that 131,000 BTUs are required to make one gallon of ethanol, but one gallon of ethanol has an energy value of only 77,000 BTUs; thus "Every time you make one gallon of ethanol, there is a net energy loss of 54,000 BTU." He estimates that ethanol production costs \$1.74 per gallon, compared to 95 cents to produce a gallon of gasoline.

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See also

- *UTTU*, Vol. 14, No. 4, July/August 2000, "Special issue on ethanol."
- *Health, Environmental and Economic Impacts of Adding Ethanol to Gasoline in the Northeast States*, July 2001; <http://www.nescaum.org/committees/ethanol-report.html>.
- *Environmental Consequences of Increased Use of Ethanol and Alkylates in California Fuels*, 2001; <http://www-erd.llnl.gov/ethanol/>.



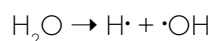
Research notes

Sonolytic Destruction of Methyl tert-Butyl Ether by Ultrasonic Irradiation: The Role of O₃, H₂O₂, Frequency and Power Density

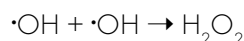
Kang, J.W., Hung, H.M., Lin, A. and M. Hoffmann, *Environmental Science and Technology*, Vol. 33, No. 18, 1999; <http://www.pubs.acs.org>.

Kang and others (1999) used ultrasound to treat MTBE-contaminated waters. Ultrasonic waves consist of compression and rarefaction cycles that produce cavitation bubbles in liquid solution. "After several compression cycles, the cavitation bubbles collapse violently and adiabatically with extremely high temperatures up to 5,000° K and pressures of 975 bar. Under these extreme conditions, volatile chemical compounds are destroyed by direct pyrolysis reactions and indirectly by reactions with H·, ·OH, O· and H₂O₂." Adding ozone into the system often enhances rate of contaminant destruction. As ozone decomposes in cavitation bubbles, ·OH forms. In addition, ozone may react directly with substrates.

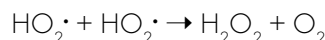
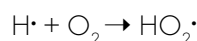
Researchers defined sonolytic degradation of MTBE to be a pseudo-first-order kinetic. They also investigated the effect of variable frequencies on peroxide production and used hydrogen peroxide production as a direct indicator of free radical production. Hydrogen peroxide is produced during the sonolysis of water, with hydrogen atoms and hydroxyl radicals formed during the pyrolytic decomposition of water:



Hydroxyl radicals can recombine to form hydrogen peroxide:



If O₂ is present in the vapor phase of the bubble, peroxide can also be produced via the production of the hydroperoxyl radical as follows:



Researchers discovered that MTBE degradation was enhanced with an ultrasound at 205 kHz and the addition of ozone. The combination of ozone and sonolysis was more effective in degrading MTBE than ultrasound or O₃ alone.

Efficacy of Bacterial Bioremediation: Demonstration of Complete Incorporation of Hydrocarbons into Membrane Phospholipids from *Rhodococcus* Hydrocarbon-Degrading Bacteria by Electrospray Ionization Fourier Transform-Ion Cyclotron Resonance Mass Spectrometry

Rodgers, R.P., Blumer, E.N., Emmett, M.R. and A.G. Marshall, *Environmental Science & Technology*, Vol. 34, No. 3, 2000; <http://www.pubs.acs.org>.

How can we determine how completely bacteria metabolize hydrocarbons? Bacteria have three options:

- not to metabolize hydrocarbons
- to metabolize them incompletely
- to mineralize them, i.e., break hydrocarbons completely for biosynthesis and/or respiration to CO₂ and H₂O

Rodgers and others (2000) offer a "simple, new, rapid method for determining the extent of mineralization of phospholipids (as well as their fatty acid and headgroup constituents) by a bacterial bioremediation candidate, *Rhodococcus rhodochrous*... Prior attempts to establish unequivocally the mineralization of hydrocarbon have relied on the following methods:

- radioactive- or stable-isotope-labeled growth substrates
- monitoring ratios of naturally occurring carbon isotopes
- using mass spectrometry as a structural analysis technique for biological membrane lipids and high-sensitivity isotope ratio or low-resolution mass analysis"

Researchers chose *Rhodococcus rhodochrous* because it can consume n-alkanes and cleave organic C-S bonds, useful for future studies of biodesulfurization.

Researchers examined the following:

- bacterial growth on minimal media containing a specified carbon source, either natural abundance 99 percent ¹²C or enriched 99 percent ¹³C
- lipid extraction
- subjection of the extract to ESI (electrospray ionization) negative-ion FT-ICR MS
- determination if ¹³C-enriched hydrocarbon incorporation is complete; if so, then the mass of the parent ion will increase and the ¹³C isotopic distribution pattern will be reversed
- obtaining the identities of the constituent fatty acids and polar headgroup by collisional dissociation (MS/MS); extent of ¹³C incorporation is determined individually

Rodgers and others (2000) reported that "mineralization of hexadecane and octadecane hydrocarbon contaminant by *Rhodococcus rhodochrous* was confirmed through the use of ¹³C-enriched hexadecane and octadecane growth substrates. Interestingly, although the food source was C₁₆ and C₁₈ hydrocarbons, we observed bacterial synthesis of phospholipid with C₁₆ and C₁₉ fatty acids. The present method could obviously be used to test for mineralization of hydrocarbons of other lengths, with or without branching, with or without double bonds. The method is definitive, rapid, and simple, requiring only a simple extraction. We therefore propose that ESI FT-ICR MS and MS/MS provide an attractive method for rapid characterization of bacterial phospholipids (to the level of elemental composition of headgroup and fatty acid side chains) as a test for the extent of bioremediation of hydrocarbons (e.g., gasoline, diesel fuel, kerosene, etc.) by a candidate microorganism."

Fate of Crude Oil by the Combination of Photooxidation and Biodegradation

Dutta, T.K. and S. Harayama, *Environmental Science & Technology*, Vol. 34, No. 8, 2000; <http://www.pubs.acs.org>.

Dutta and Harayama analyzed crude oil in seawater for its biodegradation and photooxidation potential. Their laboratory experiments lasted 8 weeks (biodegradation) and 4 weeks (photooxidation). They took samples of seawater from Kamaishi Bay, Japan, and added to it light Arabian crude oil and an autoclaved solution. This solution was cultivated for various time periods and then hydrocarbons were analyzed by GC-MS.

To analyze for photooxidation effect, researchers dropped 50 milligrams of crude oil into a glass Petri dish and set it in a ventilated chamber with a controlled temperature of 20° C. With four tin-halide lamps, four high-pressure mercury lamps, four argon lamps and a heat-absorbing filter, they produced artificial sunlight and an emission spectrum similar to that of natural sunlight.

To estimate biodegradation extent, researchers examined abundance of alkanes and aromatics; hopanes, crude oil components that are resistant to both biodegradation and photooxidation, were analyzed as a control. Crude oil subjected to photooxidation preferentially lost the lower-molecular-weight compounds, and this loss was greater than for the crude oil subjected to biodegradation.

Gravimetric analyses indicated that 28 percent of the crude oil had been biologically degraded in 8 weeks, with most of the hydrocarbons (alkanes) mineralized to CO₂ and H₂O. GC-MS analyses indicated an almost complete depletion of alkanes and naphthalene derivatives and less extensive elimination of other components.

In contrast, the photooxidized oil increased in weight, partially in response to incorporation of oxygen atoms. Researchers also noted an increase in the C₁₄ to C₂₄ n-alkanes, pristane and phytane. The n:hexane to benzene content was reduced from 30 percent to 2.9 percent. "When the photooxidized oil was subjected to biodegradation, 36 percent in weight of its components was eliminated." Another 8 weeks of biodegradation brought only a 2-3 percent reduction in weight.

Researchers concluded that more than 40 percent of the n-hexane fraction and about one-third of the hexane:benzene fraction were biodegraded. Photooxidation transformed most of the aromatics to polar fractions and, in addition, increased the biodegradative potential, leading to 36 percent of biological mineralization in contrast to 28 percent without photooxidation.

Free-Product Recovery of Petroleum-Hydrocarbon Liquids

Charbeneau, R.J., Johns, R.T., Lake, L.W. and M.J. McAdams III, *Ground Water Monitoring and Remediation*, Summer, 2000; <http://www.ngwa.org>.

This paper describes the use of recovery wells and vacuum-enhanced systems for free-product removal. Once an investigator has determined how much LNAPL (light nonaqueous-phase liquid) is recoverable, he/she must then decide the appropriate technique and pumping rate. "Although these techniques are in widespread use, few guidelines are available on the potential (optimal) pumping rates for removing both ground water and free hydrocarbon. As a result, recovery wells may not be operating efficiently, thus prolonging remediation times or causing unnecessary expenditures for additional recovery wells."

At present, optimal pumping rates have not been identified for free-product recovery systems. Low pumping rates may lengthen remediation times, while high rates may cause hydrocarbons to be smeared into deeper soils below the original water table. "When this occurs, there is an increase in the volume of soils with residual hydrocarbon contamination and a resulting reduction in the volume of recoverable hydrocarbon liquid. This may increase long-term remediation costs. Excessive pumping also produces large volumes of water that must be treated and discharged."

Charbeneau and others (2000) describe technologies for petroleum hydrocarbon recovery, develop models for liquid hydrocarbon recovery, give estimations of parameters and variables, describe effective LNAPL layer saturation and relative permeability, give estimations of LNAPL recovery times, evaluate a liquid free-product hydrocarbon recovery model, and give an example and design of a free-product recovery system.

A Compartmentalized Solute Transport Model for Redox Zones in Contaminated Aquifers

Abrams, R.H. and K. Loague, *Water Resources Research*, Vol. 36, No. 8, 2000; <http://www.ngwa.org>.

The geochemistry outside a contaminant plume differs vastly from the geochemistry inside a plume. Redox zones develop where "oxidation of dissolved organic carbon (DOC) occurs via sequential, microbially mediated redox reactions that differ widely in the amount of energy liberated by the reactions." The redox-sensitive compounds, known as electron acceptors and donors, include dissolved oxygen, nitrate, dissolved manganese and iron. The microbial consortia that can mediate a higher-energy reaction will dominate over other consortia because the energy yields differ so greatly. For instance, aerobic biodegradation will occur until all dissolved oxygen is depleted, then suboxic and/or anoxic zones form. "The sequential process continues, with each stage utilizing successively less energetic reactions, until all the available DOC or electron acceptors are depleted." The ability to biodegrade many compounds depends on redox zone conditions; naphthalene, for instance, biodegrades under aerobic conditions but biodegrades only very slowly, if at all, under anaerobic conditions.

Abrams and Loague (2000) developed a model, COMPTRAN, which links geochemical reactions with solute transport. COMPTRAN (compartmentalized solute transport model) "can accommodate any number of kinetic reactions that compete for dissolved organic carbon without the use of empirical reaction inhibition. Each reaction can have its own rate parameters and different kinetic formulations... A chief advantage of the compartmentalized approach is that kinetic constraints are embedded within a thermodynamic framework. This allows a redox reaction that yields sufficiently lower energy to be inhibited automatically in the presence of a higher-energy reaction. The compartmentalized approach therefore does not need empirical or ad hoc approaches to reaction inhibition."

"A disadvantage of the compartmentalized approach is that redox reactions are considered to be equilibrium reactions for a part of each time step. This is done to check the thermodynamic feasibility of the lower-energy redox reaction inhibitions but not necessarily to control reaction progress."

See also the authors' companion paper, "A Compartmentalized Solute Transport Model for Redox Zones in Contaminated Aquifers, 2: Field-Scale Simulations," *Water Resources Research*, Vol. 36, No. 8, 2000; <http://www.ngwa.org>.

Inhibition of Hydroxyl Radical Reaction with Aromatics by Dissolved Natural Organic Matter

Lindsey, M.E. and M.A. Tarr, *Environmental Science & Technology*, Vol. 34, No. 3, 2000; <http://www.pubs.acs.org>.

Hydrophobic pollutants, such as hydrocarbons, absorb to hydrophobic sites of dissolved natural organic matter (NOM). When this happens, pollutants are less available to remediation techniques. As Lindsey and Tarr state: "Although partitioning to these microenvironments has been studied with respect to pollutant transport and bioavailability, little effort has been made to understand how partitioning affects chemical reactivity of pollutants." Researchers studied chemical reactivity of aromatic compounds using fluvic and humic acids as NOM with respect to formation of hydroxyl radicals in the Fenton reaction. The Fenton reaction is $\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{HO}\cdot + \text{HO}\cdot$.

The hydroxyl radical reacts with the pollutant, degrading it; however, because the radical is non-selective, it can react with NOM, which can be a significant sink for the radical and decrease remediation efficiency. "Furthermore the presence of iron-binding compounds, such as NOM, can alter the rate constant for the reaction above or can alter the redox cycling of iron and thereby change the formation rate of hydroxyl radical." Laboratory experiments confirmed these views: "The presence of dissolved natural organic matter dramatically hinders degradation of hydrophobic compounds, even when the NOM is present at concentrations too low to significantly scavenge hydroxyl radical...Although this study utilized only dissolved NOM, it is likely that solid NOM (e.g. soil or sediment) would have even more dramatic effects." Researchers recommend that "devising more effective methods to deliver reactive species to the microenvironmental site of pollutants is necessary to improve reactive, transient-based remediation techniques."

NAPL dissolution in heterogeneous systems: an experimental investigation in a simple heterogeneous system

Nambi, I. and S.E. Powers, *Journal of Contaminant Hydrology*, Vol. 44, 2000; <http://www.elsevier.com/locate/jconhyd>.

Researchers conducted a two-dimensional cell dissolution experiment to identify mass flow parameters of NAPL (nonaqueous-phase liquid). The cell consisted of well-defined coarse lenses contaminated by NAPL surrounded by a clean, fine sand matrix. Researchers varied grain size, initial NAPL saturations, and size and number of coarse lenses. They found that three factors affected the system's mass transfer behavior:

- variability in the effective permeability affects the relative volume of water flowing through the NAPL source zone and extent of dilution of contaminated water with clean water around the source zone
- the perimeter surface area of the NAPL source zone affects the total interfacial area for mass transfer, especially important during the early phases of the experiment when there is little flow of water through this zone
- within the NAPL source zone, decreased mass transfer rates due to limited interfacial area or increased aqueous-phase flow rates become the overall rate-limiting factor

Assessing Long-Range Transport Potential of Persistent Organic Pollutants

Beyer, A., Mackay, D., Matthies, M., Wania, F. and E. Webster, *Environmental Science and Technology*, Vol. 34, No. 4, 2000; <http://www.pubs.acs.org>.

Researchers present an analysis of the factors that control the potential for long-range transport (LRT) of persistent organic pollutants and estimate a characteristic travel distance (CTD) or half-distance for substances in soil or water. Several modeling approaches have been suggested for assessing LRT, but "no simple relationship is expected between LRT potential and concentrations measured in the environment since concentrations are affected by the amounts emitted." Beyer and others (2000) derived a relationship between overall persistence and CTD of a substance in air or water. They studied 18 chemicals (including benzene), taking into account temperature, mode of entry, partitioning and degradation data and emissions. This projected data was compared to chemicals monitored in remote regions.

Hydrogen Isotope Fractionation During Methanogenic Degradation of Toluene: Potential for Direct Verification of Bioremediation

Ward, J.A.M., Ahad, J.M.E., Lacrampe-Couloume, G., Slater, G.F., Edwards, E.A. and B. Sherwood Lollar, *Environmental Science & Technology*, Vol. 34, No. 21, 2000; <http://www.pubs.acs.org>.

To confirm hydrocarbon biodegradation, field workers need to obtain accurate mass balances of contaminants, electron acceptors and breakdown products to separate biodegradation processes from physical processes such as sorption and dilution. This data is difficult if not at times impossible to obtain. Another way to confirm hydrocarbon biodegradation is to analyze carbon and hydrogen isotope fractionation by using a new technique, compound-specific stable isotope analysis (CSIA), which has the potential to give direct indication of biodegradation.

According to Ward and others (2000), "Recent studies evaluating the magnitude of carbon isotope fractionation produced during biodegradation of aromatic hydrocarbons have documented heavy isotope (^{13}C) enrichment in the residual contaminant approximately an order of magnitude smaller than those reported here for ^2H . The very large isotopic enrichment in ^2H suggests that, under anaerobic conditions, compound-specific hydrogen isotope analysis may provide a more reliable means of validating intrinsic bioremediation of aromatic hydrocarbons than stable carbon isotope analysis...Relatively insensitive to biodegradation by mixed consortia, stable carbon isotope values may provide information about different sources of contaminant, while hydrogen isotope values provide an assessment of the degree of attenuation due to biodegradation."

Researchers concluded: "the dramatic isotope fractionation in the hydrogen isotopic value of residual toluene during anaerobic biodegradation indicates that hydrogen isotope analysis has the potential to be a powerful diagnostic tool for identifying and monitoring intrinsic biodegradation in the field. In fact, if the relatively insensitive behavior of stable carbon isotopes with respect to biodegradation by mixed consortia...is upheld, combined stable carbon and hydrogen isotopic analysis offers a unique opportunity for field investigations."

Examining Bacterial Transport in Intact Cores from Oyster, Virginia: Effect of Sedimentary Facies Type on Bacterial Breakthrough and Retention

Fuller, M.E., Hailiang, D., Mailoux, B.J., Onstott, T.C. and M.F. DeFlaun, *Water Resources Research*, Vol. 36, No. 9, 2000, pgs. 2417-2431; <http://www.agu.org>

Researchers studied how sediment properties affected bacteria transport in three cores from three different facies. The three facies examined were cross-stratified (CS), horizontally stratified (HS) and shelly gravelly (SG). The field site (in Oyster, Virginia), an established site for bacterial transport research, has been characterized extensively in geological and hydrologic terms. In other words, researchers were familiar with the grain sizes, porosities, permeabilities and the metal oxyhydroxides. Fuller and others (2000) obtained intact cores with only minimal disturbance of sediments. Researchers set up an intact core experiment whereby artificial groundwater containing either a chloride tracer or bacteria was introduced into the core, and effluent was collected. Before injecting the bacteria, a conservative chloride tracer was added and a breakthrough curve was generated. "Because chloride is nonreactive, it is used to compare interstitial particle velocities to the advective velocities of pore fluids" (Fuller and others, 2000). The added bacteria strain, isolated from Oyster, Virginia, is a mobile, gram-negative rod that was subsequently cultured and radiolabeled. The experiments were performed using actual groundwater flowing at field-relevant, forced-gradient flowrates.

"A major goal of these experiments was to examine bacterial transport in intact sediment cores and account for all the cells that were injected into the cores by analyzing both the core effluent and the core sediment. Total effluent and sediment recoveries of [the bacteria] from the three cores were approximately 60 percent, even after incorporation of corrections for respiratory losses of ^{14}C and analytical errors. The inability to account for 100 percent of the added radioactivity could be attributed to actual losses of label through respiration or to the inability to accurately count the radiolabel in the different samples...grinding the sediment prior to analysis did yield dpm counts that were approximately 1.6- to 2.1-fold higher than unground sediment...therefore it seems reasonable that most of the missing radioactivity is being retained in sediment-associated biomass that is not accurately counted using the current sediment scintillation protocol" (Fuller and others, 2000).

Factors controlling bacterial breakthrough include

- flow rate
- grain size
- grain surface-cell interactions
- preferential flow paths through macropores

Researchers reported that “both the chloride and cells in the CS and SG cores followed similar flow paths since their respective BTCs (breakthrough curves) were similar. In contrast, the tracer and cell breakthroughs from the HS core were quite different. This could be due to the effects of cell-sediment interactions or cell exclusion. The HS core had the highest amount of metal oxyhydroxides, which could lead to greater electrostatic interactions between cells and sediment surfaces. In addition, the abundant Al and Fe hydroxides in the HS core are likely to have micropores that could discriminate between the passage of bacteria and the tracer” (*Fuller and others, 2000*).

Researchers concluded:

- for all cores, bacterial cells were generally retained near the point of introduction
- cell densities decreased along the core length
- cell densities along the length of the HS core exhibited the steepest rate of decline, attributable to the HS core’s higher metal oxyhydroxide content and smaller mean grain size
- other factors that affected transport and final distribution of bacterial cells included grain size distribution, porosity, metal oxyhydroxide content and biological factors such as percent adhesion of injected cells and existence of subpopulations with different collision efficiencies
- the decrease in collision efficiency along a core length indicates that injected bacteria are actually composed of two or more subpopulations possessing different collision efficiencies
- collision efficiencies among the different cores are directly proportional to metal oxyhydroxide content
- any collision efficiency calculated from the retained bacteria in the sediment reflects a combination of both population heterogeneity of the injected bacteria and effect of the metal oxyhydroxides

Evaluation of Vadose Zone Biodegradation of BTX Vapors

Hers, I., Atwater, J., Li, L. and R. Zapf-Gilje, *Journal of Contaminant Hydrology*, Vol. 46, 2000; <http://www.elsevier.com/locate/jconhyd>.

Hers and others (2000) evaluated BTX biodegradation processes at a former petrochemical plant near Vancouver, British Columbia. Their multi-year study included

- baseline analyses of soil samples
- soil gas monitoring below and adjacent to a building (greenhouse)
- semi-continuous monitoring of O₂
- semi-continuous monitoring of pressure below the slab
- vertical profiling of BTX vapors
- monitoring of carbon dioxide and moisture content
- monitoring of temperature and barometric pressure
- in-situ respiration tests

Using measured first- and second-order BTX degradation rates, they developed a bi-linear method for approximating Monod-kinetics.

Samples were obtained using a Geoprobe™ sampler. The site consists of fill underlain by native silt, sandy silt to fine sand with trace organic matter, underlain by dredged river sand. Depth to water table is 1.5 to 2.5 m below ground surface. “Releases of BTX from sources removed from the study site and lateral migration on the water table have resulted in an extensive zone of residual nonaqueous phase liquid (NAPL). The NAPL is distributed vertically over an approximate 1-m interval, which corresponds to the approximate water table fluctuation.”

In particular, researchers were interested in the soil vapor transport pathway to indoor air; however, the processes and factors affecting this pathway are not completely known. For instance, consider first the presence of a building that limits oxygen diffusion and affects biodegradation. “Oxygen replenishment will be a function of the diffusivity and permeability of near surface soils and the subsurface building structure and the gradients driving these processes. Advective transport of soil gas through shallow soil can occur as a result of changes in atmospheric pressure and temperature.” The building will also eliminate surface water infiltration and promote long-term drying and may compromise biodegradation processes, which studies suggest are negatively impacted in low-moisture conditions.

Hers and others (2000) point out that "Diffusion, sorption and biodegradation, for non-recalcitrant VOCs, are generally thought to have the most significant effect on VOC fate and transport within the vadose zone. Biodegradation is an important natural attenuation mechanism since it is the only process whereby there is a reduction in total hydrocarbon mass. More than 200 species of bacteria, yeast, and fungi capable of degrading petroleum hydrocarbons have been identified, with *Pseudomonas* spp. and *Corynebacterium* spp. thought to be the two major bacterial agents. Aerobic biodegradation of petroleum hydrocarbons will occur in the vadose zone providing there is sufficient O₂, indigenous microbes that produce enzymes capable of degrading the compound of interest, soil moisture, nutrients and appropriate pH, temperature and salinity conditions and no inhibiting conditions... anoxic and/or anaerobic biodegradation can also potentially occur in the vadose zone depending on types of electron acceptors present, pH conditions and oxidation-reduction potential."

Researchers concluded the following:

- O₂ monitoring beneath the slab showed diurnal changes in O₂ concentrations due to temperature fluctuations and daylong to weeklong O₂ trends that appear to be correlated with barometric pressure, but effects were limited to a 0.3-m depth beneath the slab
- diffusive O₂ transport is primarily controlled by moisture content and varies over several orders of magnitude
- building characteristics and size and surface cover significantly affect diffusive O₂ transport
- BTEX biodegradation rates are significant in this setting and predictive models should include the possibility of bioattenuation
- biodegradation modeling should include soil types, possible seasonal variation in moisture conditions, potential construction of barriers that would reduce O₂ transport to subsurface soils and advective processes
- vapor-phase BTX and oxygen transport are sensitive to partial diffusion barriers, such as building foundations
- depressurizing within a building and advective transport has a potentially significant effect on BTX fate in soil below

Determination and Distribution of Diesel Components in Igneous Rock Surrounding Underground Diesel Storage Facilities in Sweden

Loren, A., Hallbeck, L., Pedersen, K. and K. Abrahamsson, *Environmental Science & Technology*, Vol. 35, No. 2, 2000; <http://www.pubs.acs.org>.

Researchers investigated a storage facility that consisted of six vaults situated 50 m below ground surface and beneath the water table. The vaults are unlined, thus stored diesel can be in contact with the fractured igneous bedrock in which the vaults are stored. Continuous groundwater pumping creates a cone of depression that traps diesel and hinders outward diesel migration. During the fill-up phase, however, the potential exists for diesel to migrate into the fractured igneous rock. Initial investigation of the area revealed diesel contamination all along the 50-m cores that were taken and investigators estimated that several tons of diesel had been released into the rock.

"Because of the enormous risk of explosions associated with opening and cleaning of the vaults, together with very high costs, it was decided that all sampling and cleaning processes for other storage facilities had to be done from the ground. To be able to assess the fate of diesel components in the surrounding bedrock, both a reliable drilling method and a method for the determination of a wide range of diesel components were needed."

Thus, researchers developed a novel drilling method, triple-tube core drilling, to investigate the diesel-contaminated rock. Standard core drilling would have smeared diesel along the drill core, contaminating the samples. The analytical procedure they used involved dissolving the silicate portion of the igneous rock by immersion in hydrofluoric acid, converting the solid rock phase into a solution. Analytes can be extracted into an organic phase prior to GC-MS analysis.

From analysis of several cores, researchers concluded that the "distribution of diesel components in rock is very difficult to predict. This is mainly because of difficulties in determining the major flow direction of groundwater and in describing and quantifying microfractures in hard rock. Our core mapping did not show any specific pattern of the intersected fractures either in vertical or horizontal directions of the facility. Contaminated areas in igneous rock will therefore not show up as contamination plumes."



Information sources

U.S. EPA publications and information

Publications that can be viewed or downloaded at <http://clu-in.org/techpubs.htm> include

- *Abstracts of Remediation Case Studies, Volume 5* (EPA 542-R-01-008)
- *A Citizen's Guide to In-Situ Thermal Treatment Methods* (EPA 542-F-01-012)

EPA Requirements for Quality Management Plans (EPA-240-B-010-002) can be viewed or downloaded at <http://www.epa.gov/quality/qs-docs/r2-final.pdf>.

Technical and Regulatory Guidance for In-Situ Chemical Oxidation of Contaminated Soil and Groundwater (ISCO-1) can be viewed or downloaded at <http://www.itrcweb.org/ISCO-1.pdf>.

U.S. EPA Web sites

Design for the Environment, <http://www.epa.gov/opptintr/dfe>

MTBE Treatment Case Studies, <http://www.epa.gov/swrust1/mtbe/mtberem.htm>

New Chemicals Program, <http://www.epa.gov/opptintr/newchems>

Publications of note

Books from Battelle, <http://www.battelle.org/bookstore> (800-451-3543) include

- *Biopile Design, Operation and Maintenance Handbook for Treating Hydrocarbon-Contaminated Soils*
- *Carbon Sequestration in Soils: Science, Monitoring and Beyond*
- *Cost-Effective Remediation and Closure of Petroleum-Contaminated Sites*
- *Helping Researchers Write...So Managers Can Understand*
- *International In-Situ and On-Site Bioremediation Symposia*
- *Options for Remote Monitoring and Control of Small Drinking Water Facilities*
- *Permeable Barriers for Groundwater Remediation*
- *Pollution Prevention Opportunity Assessments for Research and Development Laboratories*

- *Principles and Practices of Bioslurping*
- *Principles and Practices of In-Situ Chemical Oxidation Using Permanganate*
- *Procedure Writing: Principles and Practices, Second Edition*
- *Soil Bioventing: Principles and Practice*
- *Vadose Zone Science and Technology Solutions*

Chemical and Biological Sensors for Environmental Monitoring, published by Oxford University Press, <http://www.oup-usa.org/>, is part of an American Chemical Society Symposium on sensors, including chemical-, enzyme- and protein-based-sensors.

Chemistry and Physics of Carbon, published by Marcel Dekker, <http://www.dekker.com>, examines the scientific and technological issues related to environmental applications of carbon materials.

Effects of Changing Climate on Weather and Other Human Activities, published by University Science Books, <http://www.uscibooks.com/>, gives an explanation of the differences between weather and climate.

The Environmental Pendulum: A Quest for the Truth about Toxic Chemicals, Human Health and Environmental Protection, published by University of California Press, <http://www.ucpress.edu/press>, gives an overview of 20 years of waste management.

Gas Chromatography—Olfactometry: The State of the Art, by Oxford University Press, <http://www.oup-usa.org/>, gives 16 analyses on aspects of GC including trace compound analysis, flavor, aroma, standards and measurements.

Groundwater Chemicals Desk Reference is available from CRC Press, 800-272-7737.

Introduction to Risk Analysis: A Systematic Approach to Science-Based Decision Making, by D.M. Byrd and C.R. Cohen, is available from the Government Institutes Division, <http://www.govinst.com/>.

Physical Science: What the Technology Professional Needs to Know, published by John Wiley, <http://www.wiley.com>, explains basic physics and chemistry principles.

A Systems Approach to the Environmental Analysis of Pollution Minimization, Lewis Publishers, 800-272-7737, describes how mass and energy balances are used to quantify pollution extent and its sources.

Web sites

New Ideas in Pollution Regulation,

<http://www.worldbank.org/nipr>

The Chemical Industry Home Page,

<http://www.neis.com/db/category/cat166.asp>

The Information Center for the Environment, University of California-Davis, <http://ice.ucdavis.edu>

The National Wind Technology Center,

<http://www.nrel.gov/wind>

U.S. Global Change Data and Information Systems,

<http://globalchange.gov>

U.S. Global Change Research Program,

<http://www.usgcrp.gov/usgcrp/new.htm>

Additional papers, old and new

"Evaluating Environmental Chemistry Textbooks," by R. A. Hites, gives a fairly comprehensive review of 14 chemistry books, *Environmental Science & Technology*, January 1, 2001; <http://www.pubs.acs.org>.

"Natural Attenuation for Ground Water Remediation," <http://www.epa.gov/superfund/resources/gwdocs/monit.htm>.

"Occurrence and Distribution of Methyl Tert-Butyl Ether and other Volatile Organic Compounds in Drinking Water in the Northeast and Mid-Atlantic Regions of the United States, 1993-98," *Water Investigations Report 00-4228*, is available on the U.S. Geological Survey Web site under "What's new at our site":

http://sd.water.usgs.gov/public_naw/vocns/.

"Phytoremediation Technology Evaluation Report," TE-98-01, by J.L. Schnoor,

<http://www.gwrtac.org/html/topics/phytorem.htm>.

"Recommended Readings for Environmental Site Investigations," by D.A. Stirling, is a list of literature related to environmental site investigations; *Practice Periodical of Hazardous, Toxic and Radioactive Waste Management*, January 2000; <http://ojps.aip.org/hzo/>.

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