



# Underground Tank Technology Update

Vol. 18, No. 1 January/February 2004



uttu.engr.wisc.edu

Department of Engineering Professional Development

Underground Tank Technology Update is an electronic bimonthly publication of the University of Wisconsin-Madison, Department of Engineering Professional Development. UTTU supplies useful information to federal, state, and local officials working with groundwater technology and to other interested technical specialists.

UTTU is funded by the U.S. EPA under cooperative agreement No. 82933001 to the University of Wisconsin-Madison, which is responsible for its preparation. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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.

## Advisory Board

**Gilberto Alvarez**, Environmental Engineer  
OUST, U.S. EPA, Region 5, Chicago, Illinois

**Bruce Bauman**, Research Coordinator  
Soil/Groundwater, API, Washington D.C.

**Lynn DePont**, Grants Project Officer, OUST, U.S. EPA,  
Washington D.C.

**Louis Fournier, Ph.D.**, Chemist and President  
STAR Environmental, Inc., Chadds Ford, Pennsylvania

**Jeff Kuhn**, DEQ, Petroleum Section, Helena, Montana

**Joseph Odencrantz**, Principal  
Tri-S Environmental, Costa Mesa, California







**Phil O'Leary**, Professor, Department of Engineering Professional  
Development, UW-Madison

**Gerald W. Phillips**, U.S. EPA, Region 5, Chicago, Illinois

## Staff

John T. Quigley	Project Director
Pat Dutt	Geologist/Writer
Darrell Petska	Copy Editor
Debbie Benell	Program Assistant

## Brief article summaries

-  **Delaware's experience with tertiary-butyl alcohol.....2**  
Not until recently did Delaware designate TBA as a contaminant of concern. This article describes the efforts undertaken to establish a drinking water action level for TBA in order to develop risk-based screening levels (RBSLs) for the compound.
-  **Gasoline releases .....4**  
Wanting to create a database for risk assessment of fuels and validation of numerical models, scientists set up an experiment to investigate the fate of spilled gasoline containing ethanol and MTBE. The experiment proceeded in the unsaturated zone in a temperate region and relied on a field lysimeter equipped with soil gas and groundwater sampling ports to collect data. Researchers created a setup in a homogeneous porous medium from which they could quantify transport of compounds (MTBE, ethanol, benzene) to the atmosphere and groundwater. They monitored first arrival in groundwater, disappearance in groundwater and mass balances and assessed biodegradation.
-  **Review of MTBE bioremediation .....6**  
This article summarizes a comprehensive study by Fiorenza and Rifai on MTBE biodegradation. Among the topics discussed are MTBE degradation pathways, laboratory studies, aerobic biodegradation by mixed cultures, aerobic biodegradation by pure cultures, cometabolism by alkane oxidizers, biodegradation of MTBE in mixtures, and laboratory studies of anaerobic biodegradation.
-  **UST testing, part II .....9**  
The first part of this article (in UTTU Vol. 17, No. 5, 2003) introduced tank testing and described some tests normally performed on USTs. The second part describes tank deflection, tank-hole liners, detectors, indicators, monitors, overfill protection devices, precision testing and the significance of temperature.
-  **Research notes.....12**  
In this issue, research notes include articles on decontamination protocols, bacterial production in a groundwater circulation well, CTP-hole closure, a model for air quality, LUST cleanup methods, partition tracer testing, hydrocarbon testing and retention.
-  **Information sources.....15**  
Information sources give Web sites of recent publications.

**Free Subscription** To receive this electronic newsletter, e-mail [Debbie Benell](mailto:benell@epd.engr.wisc.edu) (benell@epd.engr.wisc.edu) or call 608-263-7428. There is no cost to subscribers.



## Delaware's experience with tertiary-butyl alcohol

Not until recently did Delaware designate TBA as a contaminant of concern (Fischer, 2003). This article describes the efforts undertaken to establish a drinking water action level for TBA in order to develop risk-based screening levels (RBSLs) for TBA.

### TBA presence in Delaware

Between 40 and 50 sites in Delaware have measurable concentrations of tertiary-butyl alcohol, or TBA. Characteristics of TBA occurrence in Delaware include the following:

- TBA always occurs with MTBE
- in groundwater, TBA concentrations range from detectable levels, 5 ppb to 20 ppm; a few sites had concentrations of 100 to 300 ppm
- in soil, TBA ranged from 0.17 to 7.9 ppm

Typical concentrations of TBA in MTBE that is 95 to 98 percent pure range from 0.6 to 2 percent. In 1979 ARCO and Sun Oil Co. Delaware obtained approval from Delaware regulators to use 7.0 and 2.85 percent TBA in gasoline, but TBA had been used as a gasoline additive as early as 1969. Regulators at Delaware's Risk-Based Corrective Action Program (DERBCAP) did not require MTBE analyses at MTBE risk sites until 1998. However, "soil samples collected by consultants at the time of removal or upgrade must be analyzed for MTBE unless documentation is presented and preapproved by the UST branch that the tank was out of service prior to January 1, 1978. When MTBE is detected during the hydrogeological investigation stage (Tier 1), TBA subsequently becomes a required analyte as well for all samples collected. Should TBA become a regulated contaminant of concern (COC) in DERBCAP, the department would have to determine a date, similar

to the 1978 date for MTBE, from which to require sampling" (Fischer, 2003).

Since DERBCAP incorporated, about 70 percent (200 sites) of groundwater LUST sites (operating and non-operating) have detected MTBE. Before the requirement for oxygenate analysis was implemented, however, about 830 gasoline-contaminated sites were closed. Because every MTBE site is a potential TBA site, these closed sites are a cause for concern.

### Established aesthetic levels and health effects of TBA

Groundwater regulators establish MCLs (maximum contaminant levels), action levels and secondary action levels to protect the public from contaminated water and ensure that aesthetic quality of the resource is maintained. TBA "has an established odor threshold of 21 ppm, which is likely to be significantly higher than health-based concentrations" (Fischer, 2003). For comparison, MTBE's taste and odor threshold is 5.3 to 30 ppb, or three orders of magnitude smaller than its health-based level.

To define health-based concentrations, scientists rely on toxicological studies. TBA toxicological studies are few, and include the following acute studies:

- a 1952 study found the oral LD50 (term explained below) in rats to be 3,500 mg/kg
- a 1972 study identified the oral LD50 in rabbits to be 3,600 mg/kg
- a 1979 study found mouse LD50, through direct injection to the peritoneal cavity, to be 441 mg/kg

LD50 is the "amount of material, given all at once, which causes the death of 50 percent of a group of test animals" (<http://www.ccohs.org/oshanswers/chemicals/>)

A two-year chronic study of rats involved giving 60 male and 60 female rats drinking water with 0, 1.25,

2.5 or 5 mg/ml (male rats) and 0, 2.5, 5 and 10 mg/l (female rats) for 13 weeks or two years. "The study concluded that after two years there was some evidence of carcinogenic activity in the male rats based on the combined accumulation of malignant and benign tumors in the kidneys. There was no evidence, however, in female rats receiving 2.5, 5, or 10 mg/ml TBA. Male mice developed the combined accumulation of malignant and benign tumors in the thyroid gland while female mice showed evidence of increased incidences of benign tumors developing in the thyroid glands as well. Based on the study, scientists concluded that male rats and female mice showed evidence of a carcinogenic response to TBA. Because it is a potential carcinogen, we are faced with the task of extrapolating this data to human exposure limits since human data regarding TBA toxicity is nonexistent" (Fischer, 2003).

Fischer also points out that "the massive doses of TBA (2,000 to 10,000 mg/l) resulted in only limited evidence of carcinogenic responses in the male rats and female mice. In addition, in vitro and in vivo mutagenicity and clastogenicity tests performed with TBA provided no evidence of genotoxicity. TBA is therefore considered nonmutagenic."

### Field occurrence of TBA

The first documented occurrence of TBA and MTBE was in 1997 in a gasoline-contaminated aquifer in Beaufort, South Carolina. Researchers found that TBA/MTBE concentration ratios increased along the groundwater flowpath; they concluded that the increase resulted from either higher solubility of TBA or MTBE degradation to TBA. Another study in 1994 suggested that under anaerobic conditions, MTBE degraded to TBA without further degradation. A 1997 study "showed nearly stoichiometric production of TBA when MTBE was degraded using propane-oxidizing strains of bacteria" (Fischer, 2003).

Numerous other examples show TBA being generated in the field from MTBE degradation.

### TBA physical and chemical properties

Physical/chemical properties of TBA include the following:

- TBA is infinitely soluble in water by itself and out of gasoline at a volume of 0.6 and 2 percent (vol/vol)
- TBA has a low soil-water and octanol-water partition coefficient, indicating a low affinity for soil adsorption and high affinity for water
- TBA has a low affinity to partition from the aqueous to the vapor phase

These characteristics suggest that using air stripping to remove TBA from water is likely to be difficult.

### Cost of remediation

Costs for TBA remediation will depend on the TBA drinking level, which has not yet been defined. "As previously mentioned, enormous doses of TBA in drinking water barely yielded carcinogenic responses in rats and mice. Therefore, when qualitatively extrapolating to harmful human doses, one might expect to find concentrations orders of magnitude higher than those actually found at points of exposure. In such cases, TBA could not likely be a driver for the remediation and investigation. However, the calculation of action levels may incorporate uncertainty factors (UFs) that can affect the concentrations by a factor of 1/100,000. In other words, incorporating all of the UFs could turn a 5 ppm allowable exposure concentration into 0.00005 ppm. Depending on the selection of UFs, the result could be ultraconservative concentrations that will result in TBA driving the remediation and investigation" (Fischer, 2003).

Of the methods used to analyze for TBA:

- U.S. EPA method 8020A/21B gives unreliable results when used to analyze samples with low TBA concentrations; it frequently produced false positives with high concentrations of nonoxygenated gasolines
- U.S. EPA method 8021A/21B was useful as a screening tool, but not as effective as the more expensive method 8260A
- method 8021 costs \$50 to \$65
- method 8260 costs \$147 to \$233

If a Delaware site has an average of five to seven monitoring wells and is monitored quarterly, costs for 8260 analysis could be between \$2,000 and \$5,000 annually.

Fischer (2003) points out that because MTBE degrades to TBA, there is a potential for TBA to exist beyond the defined MTBE plume. "A TBA plume 20 percent longer than the MTBE plume would likely require 20 percent more sampling points, which increases costs. For example, installing two additional 4-inch monitoring wells to further characterize and monitor a TBA plume past the extent of MTBE could add nearly \$5,000 to the project cost in well construction alone."

### Remedial actions

TBA treatment will depend on action levels developed but could include the use of

- GAC (granular activated carbon)/carbon filtration
- MNA (monitored natural attenuation)

*GAC/carbon filtration.* TBA adsorption on GAC has had some successes and some failures, and its effectiveness as a treatment technology is still undecided. According to Fischer (2003), "Poor TBA adsorption could as much as double the amount of carbon used at a site and therefore increase project costs by thousands

to tens of thousands of dollars. As more carbon is being consumed, disposal/material costs and contractor time increase to maintain the system. In many cases, rising project costs may result in a reevaluation of remedial technologies."

Carbon filtration used for TBA and MTBE removal indicated that TBA detected in the effluent was likely being produced in the filter from MTBE biodegradation; therefore, use of carbon filtration as a treatment technology is questionable.

MNA. Again, reports on effectiveness disagree but rely largely on MTBE biodegradability. "At sites where TBA is recalcitrant to biodegradation, MNA becomes a function of mechanical [or physical] and chemical processes such as advection and diffusion. Without biodegradation to expedite MNA, TBA-contaminated sites are likely to take longer to remediate than sites with only MTBE and will therefore increase cost" (Fischer, 2003).

### Action levels

Delaware has no regulatory action levels for TBA. Neither has the U.S. EPA classified TBA based on carcinogenic weight of evidence. California conducted a risk assessment evaluation for TBA in drinking water and developed an interim drinking water concentration of 0.012 mg/l (12 ppb). Fischer says that "Until additional carcinogenic data become available, a full risk assessment is improbable. Therefore, Delaware may choose to adopt the California assessment or conduct its own interim assessment based on the limited data available."

He adds: "Another concern not addressed in this paper is interim decision making. Although Delaware does not yet have formal standards, TBA is being monitored closely. As a result, an interesting dilemma arises. How do state regulators handle sites with groundwater containing dissolved concentrations of TBA? For example, some sites where MTBE is the driver for remediation are being successfully remediated for MTBE through carbon

filtration but are discharging water with TBA at over 100 ppb. With no action levels established for TBA, is this acceptable or enforceable?

"Primary concerns with establishing action levels are the potential for a significant increase in project cost and the dilemma of previously closed sites. Adding TBA to a list of COCs could increase lab costs and require more effort and resources in plume delineation and remediation. On the other hand, because TBA was not previously on the COC list, nearly every gasoline release closed by state regulators did not have an analysis for TBA. At sites where MTBE concentrations dropped significantly, TBA concentrations may be significant."

Fischer recommends that the State of Delaware's Division of Public Health take one of three actions:

- review and adopt California's standard
- review and customize the California assessment based on Delaware's needs
- conduct its own risk-based assessment of TBA

He adds that "If it can be determined, quantitatively, that a 120 ppb action level poses no more of a risk (in terms of cancer) than California's 12 ppb action level, then several thousands of dollars may be saved at each TBA-contaminated site."

## Reference

Fischer, W.T., "An Evaluation of Tertiary-Butyl Alcohol for the Development of a Drinking Water Action Level in Delaware," *Ground Water Monitoring & Remediation*, Vol. 23, No. 2, 2003; <http://www.ngwa.org>

**UTTU thanks Tripp Fischer,**  
[William.Fischer@state.de.us](mailto:William.Fischer@state.de.us), for his help on this article.



## Gasoline releases

To create a database for risk assessment of fuels and validation of numerical models, Dakhel and others (2003) set up an experiment to investigate the fate of spilled gasoline containing ethanol and MTBE. The experiment proceeded in the unsaturated zone in a temperate region and relied on a field lysimeter equipped with soil gas and groundwater sampling ports to collect data. Researchers created a setup in a homogeneous porous medium from which they could quantify transport of compounds (MTBE, ethanol, benzene) to the atmosphere and groundwater. They monitored

- first arrival in groundwater
- disappearance in groundwater
- mass balances and assessed biodegradation

## Study materials, methods and sampling

Scientists filled a cylindrical field lysimeter with uncontaminated gravel and sand. The lysimeter was 1.2 m in diameter and 2.5 m in depth. A siphon, installed at 2.33 m, was used to regulate groundwater table height. Overflowing groundwater was collected, quantified and analyzed. A capillary fringe was established at 0.07 m. Contaminated sand and an aqueous fluorescein solution, mixed in a concrete mixer, were placed at a 1.2 to 1.0 m depth in the lysimeter and covered over with clean sand. Some loss of volatiles occurred. (For a visual of the lysimeter, see <http://www.mypage.bluewin.ch/hoehener/p7page.html>.)

Soil temperatures were kept between 0.5° and 8° C during the first 41 days and between 3° and 14° C from day 41 to 127. Groundwater temperature at 2.3 to 2.5 m depth ranged from 11° ± 1° C during the first 41 days to 11° to 14° C during the remainder of the test. From day 42 to day 71, a manual sprinkler supplied 5 mm of distilled water daily to the lysimeter. The top sur-

face of the lysimeter was free of snow, ice and plants. Researchers used the following instruments/procedures for analyses:

- two sampling ports in groundwater and the siphon overflow yielded groundwater samples
- an 8 cm hollow-stem auger was used to drill soil cores
- a portable sensor measured O<sub>2</sub>
- a GC-FID analyzed for CO<sub>2</sub>
- a headspace technique and GC/FID analyzed for gasoline components
- a salting-out headspace technique combined with GC-FID analyzed ethanol
- a fluorescence spectrophotometer measured fluorescein

## Vapor-phase profiles

Researchers obtained depth profiles of vapors and gases. "The maximum vapor concentrations of MTBE, ethanol, and benzene were found in the first three days at a depth of 1.1 m in the contaminated sand layer. At this depth, the vapor concentrations of these compounds later decreased because of volatilization, leaching, and/or biodegradation. Initially, vapors spread symmetrically upward and downward from the source zone, suggesting that vapor-phase diffusion was the dominant transport process and that gravity-driven advection was unimportant" (Dakhel and others, 2003).

The study also revealed the following:

- the appearance of benzene vapors at 0.1 m depth after one day
- the appearance of MTBE vapors after three days
- ethanol vapors never migrated to the surface or groundwater; highest concentration remained closely near the initial burial depth until day 127, when concentrations fell below the detection limit

- benzene vapor profiles suggested that the volatilizing source of gasoline remained in the initially contaminated sand at 1.1 m depth
- MTBE profiles were similar until day 77, when "MTBE vapor concentration profiles gradually approached linear profiles from the soil surface to the groundwater, suggesting that the groundwater became the main volatilizing force"
- O<sub>2</sub> flux cannot exclusively be attributed to aerobic microbial degradation of hydrocarbons; hydrocarbon vapor generation in the contaminant source, a small counter-flux of air, accounts for the hydrocarbon vapors diffusing to the atmosphere

In groundwater:

- MTBE concentration remained below detection limits of 20 µg/l during 9 days, increased to 4,800 µg/l on day 29, and increased to > 250,000 µg/l until day 191
- ethanol remained below the detection limit of 250 µg/l in groundwater before recharge was applied, reached a maximum of 7,200 µg/l on day 62, and fell below detection limit on day 111
- benzene remained below the 4 µg/l detection limit for 55 days, peaked on day 69 with 340 µg/l, and reached the detection limit on day 128
- the gaseous tracer CFC-113 rose above detection limit on day 14 and remained measurable until complete volatilization by day 100
- the water tracer fluorescein remained below detection limit during 62 days, then peaked on day 100 with a concentration of 0.7 µg/l
- dissolved O<sub>2</sub> was at 88 percent saturation at the start of the experiment and declined gradually to 10 to 20 percent saturation after day 55
- TBA was not found above the detection limit of 80 µg/l

- by day 191, only MTBE, isooctane and fluorescein remained in groundwater

### Soil analysis

Researchers obtained a soil core on day 191. Data analysis revealed the following:

- Sudan (IV), a tracer, was detected only between 1.0 and 1.3 m depth in the unsaturated zone
- ethanol, benzene and five other petroleum hydrocarbons had completely disappeared from the unsaturated zone
- more than 85.5 percent of the initial gasoline mass was no longer detectable in the unsaturated zone
- the remaining 14.5 percent detected between 1 and 1.3 m consisted of n-dodecane, n-decane, 1,2,4-trimethylbenzene, m-xylene, n-octane and traces of MTBE, toluene, isooctane and methylcyclohexane

### Vapor-phase transport

Researchers found the following:

- MTBE and petroleum hydrocarbon diffusion from soil to groundwater was an important and rapid transport pathway in the unsaturated sand
- ethanol vapors were completely attenuated; vapors partitioned into soil water and biodegraded
- ethanol was not sorbed because of its low octanol-water partitioning constant

A model set up by researchers indicated that

- one out of nine benzene molecules that volatilized from the buried residual gasoline was present in the soil air phase; the remaining were dissolved in the soil aqueous phase or sorbed
- one out of 20 MTBE molecules was present in the soil air phase

- one out of 2,000 ethanol molecules was present in the soil air phase; 97 percent of the ethanol partitioned into the aqueous phase

### Unsaturated zone biodegradation

After a lag phase of 6 days, biodegradation of fuel compounds to CO<sub>2</sub> began. "The maximum CO<sub>2</sub> concentrations as well as the total CO<sub>2</sub> flux to the atmosphere were about three times smaller than the ones observed in a previous experiment under warmer summer conditions without recharge... In this study, a linear profile from the atmosphere to the groundwater was observed for MTBE on day 210. The degradation product TBA was not detected in the soil gas. Also for benzene, the profiles were generally linear to a depth of 1 m, indicating slow biodegradation in the upper unsaturated zone. The highly curved depth profiles for ethanol are a result of both partitioning into soil gas and biodegradation" (Dakhel and others, 2003). Because the profiles do not represent steady-state conditions, scientists did not attempt to determine biodegradation rates.

### Capillary fringe biodegradation

Expected vs. observed benzene concentrations suggested active benzene biodegradation in the capillary fringe. "The implication of aerobic biodegradation...in the capillary fringe is illustrated by the difference in oxygen saturation, with 20 percent saturation in the groundwater and 80 to 86 percent saturation in the soil air 13 cm above the groundwater table."

### Groundwater natural attenuation

Dakhel and others (2003) found in groundwater:

- ethanol and benzene concentrations, "after reaching their highest concentrations decreased exponentially with half-life times of eight and 10 days, respectively, in groundwater"

- concentrations of MTBE and fluorescein “decreased from day 100 to day 191 rather linearly to 50 percent; decreases are attributed to dilution with recharge water of lower concentration, volatilization and degradation”
- MTBE biodegradation was slow or absent
- absence of TBA (intermediate degradation product of MTBE) also supports slow/absent MTBE biodegradation
- ethanol and benzene removal in groundwater is likely due to aerobic biodegradation
- no preferential removal of ethanol occurred as compared to benzene in groundwater
- ethanol was found to stimulate toluene biodegradation under anaerobic conditions
- absence of direct contact of gasoline with groundwater resulted in lower ethanol concentrations in groundwater and did not adversely affect benzene disappearance
- high porosity and ease of oxygen diffusion in the sandy soil favored benzene biodegradation

### Mass balance

Mass balance accounting of MTBE indicated that about 51 percent ended up in groundwater, and 49 percent volatilized to the atmosphere, again suggesting insignificant biodegradation. Researchers assert that their findings are in good agreement with numerical simulations. They point out that “ethanol may have had a negative impact on the biodegradation rate of MTBE”; however, they also state that the concurrent use of MTBE and ethanol would be unlikely. Most MTBE biodegradability studies agree that “poor MTBE biodegradability is either a result of its chemical structure or of preferential degradation of native gasoline compounds.” Because the ethanol did not volatilize or accumulate in groundwater, biodegradation is suggest-

ed as the sole removal mechanism. Volatilized benzene fractions were 31 percent while biodegraded fractions were 69 percent. Researchers also state that

- they could not account for 34 percent of the buried total mass of hydrocarbons with the methods they used
- volatilization by diffusive fluxes may have an error of 20 percent due to uncertainty in the tortuosity factor

Researchers conclude that “After 6 months the MTBE concentration in groundwater was three orders of magnitude larger than the sum of other gasoline hydrocarbons. The main conclusion of this study is that groundwater quality will be affected considerably less at small-volume release sites where MTBE-free gasoline or gasohol are spilled.”

### Reference

Dakhel, N., Pasteris, G., Werner, D. and P. Hoehener, “Small-Volume Releases of Gasoline in the Vadose Zone: Impact of the Additives MTBE and Ethanol on Groundwater Quality,” *Environmental Science & Technology*, Vol. 37, No. 10, 2003; <http://pubs.acs.org>  
See also <http://www.mypage.bluewin.ch/hoehener/p7page.html> for a visual of the lysimeter and for other papers published by the authors.



### Review of MTBE bioremediation

This article summarizes a comprehensive study by Fiorenza and Rifai (2003) on MTBE biodegradation. Among the topics discussed are MTBE degradation pathways, laboratory studies, aerobic biodegradation by mixed cultures, aerobic biodegradation by pure cultures, cometabolism by alkane oxidizers, biodegradation of MTBE in mixtures, and laboratory studies of anaerobic biodegradation.

### Overview of MTBE biodegradation

When MTBE was first recognized as a problem about 20 years ago, most researchers believed MTBE was recalcitrant. “The recalcitrance of MTBE has been attributed to its chemical structure, with the ether bond and the tertiary carbon atom responsible for the difficulty in biodegradation.” Yet, “The debate regarding MTBE’s biodegradability, especially under different environmental conditions, and about the role of biodegradation in limiting its transport in the groundwater is likely to continue for several years” (Fiorenza and Rifai, 2003). MTBE biodegradation is most successful when the environment is aerobic, although anaerobic biodegradation of MTBE is an active area of research.

### MTBE degradation pathways

MTBE degradation is contingent on cleavage of the ether bond. Ether bond energy, at 360 kJ, is relatively high. Scientists have proposed eight possible mechanisms for bond cleavage:

- oxygenative cleavage by monooxygenases
- oxidation by cytochrome (P450) monooxygenases
- hydroxyl shift
- hydrolysis
- anaerobic cleavage of methyl-aryl ethers
- oxidative mechanisms
- reductive mechanisms
- carbon-oxygen lyases

### Mixed culture aerobic biodegradation

Following is a list of studies that used mixed cultures to degrade MTBE (see Fiorenza and Rifai article in *Bioremediation Journal* for full citation of references mentioned here):

- Salanitro and others (1994) experimented with BC-1, enriched from the bioreactor sludge of a chemi-

- cal plant to degrade MTBE; "the culture oxidized  $\text{NH}_4^+$  in the culture medium to  $\text{NO}_3^-$ ; nitrification by some of the culture members seemed to stabilize MTBE degradation; when cell retention time was decreased, MTBE degradation decreased, suggesting that the MTBE degraders are slow-growing organisms" (Fiorenza and Rifai); TBA (tert-butyl alcohol) was detected as a metabolite
- Salanitro and others (1996) created microcosms using groundwater from a marketing terminal site and observed a first-order degradation rate of 0.31/day; they again used BC-1, this time to produce TBA, which was metabolized via isopropanol and acetone; MTBE did not inhibit BTEX degradation
  - Cowan and Park (1996) used an MTBE-degrading enrichment culture from a petroleum refinery wastewater treatment plant; from the culture, MTBE, ETBE (ethyl tert butyl ether), TAME (tert amyl methyl ether), TBA and TAA (tert amyl alcohol) were biodegraded at 30° C
  - Eweis and others (1998a) found a mixed microbial culture to degrade MTBE and TAME, but the culture did not degrade ETBE and DIPE (diisopropyl ether)
  - Bradley and others (1999) used labeled  $^{14}\text{C}$ -MTBE and  $^{14}\text{C}$ -TBA at a site containing BTEX, MTBE and TBA; after 105 days,  $73 \pm 14$  percent and  $30 \pm 8$  percent of  $^{14}\text{CO}_2$  from  $^{14}\text{C}$ -MTBE were recovered from aerobic microcosms of the two sites; scientists observed no mineralization but found degradation rate was lower when organic content was higher; scientists also suggested that MTBE mineralization was limited to a thin aerobic zone at the sediment surface
  - Bradley and others (2001 a), in another study, observed greater mineralization in sandy sediments than those with a higher percentage of silt and clay

- Hunkeler and others (2001) determined that 3-methylpentane could act as a cometabolic substrate that used uncontaminated Borden aquifer material, MTBE and neat 3-methylpentane
- Schirmer and others (2003) observed MTBE degradation in microcosms created from unaltered Borden aquifer material; "...all of the 50 percent transformation occurred by 68 days, and no further transformation was observed over an additional 267 days of incubation"; TBA and TBF were not detected; additional experiments studied MTBE biodegradation with respect to other substrates and biodegradation of MTBE-containing microcosms vs. TBA-containing microcosms; "authors suggested that cometabolic degradation of MTBE in the Borden aquifer, possibly using natural organic carbon as a primary substrate, was the most likely mechanism for MTBE disappearance"
- Landmeyer and others (2001), using a biofilm from a site with a history of MTBE contamination, studied MTBE biodegradation in a liquid culture; after 80 days, no MTBE remained
- Kharoune and others (2002) isolated a microbial consortium from gasoline-contaminated soil and used it to degrade MTBE, TAME and TBA; alcohol intermediates did not accumulate; MTBE biodegradation rate, 1.1 mg/l/h, remained the same "whether it was present as the sole substrate or in combination with ETBE and TAME"
- Kane and others (2001) studied the effect of oxygen addition on MTBE biodegradation

Researchers have also created laboratory bioreactors to study mixed culture aerobic MTBE biodegradation. "The types of reactors investigated have ranged from those that support attached growth of microorganisms, such as trickling filters, to those that support suspended growth, such as a stirred tank reactor. It has been hy-

pothesized that attached growth enhances the development of MTBE degraders" (Fiorenza and Rifai, 2003). Studies follow:

- Fortin and Deshusses (1999) created laboratory biotrickling filters to maintain an aerobic, MTBE-degrading microbial consortium; after 6 months of acclimatization, 97 percent of added MTBE was converted to  $\text{CO}_2$
- Eweis and others (1998b) engineered a biofilter packed with 1-cm diatomaceous earth that removed greater than 95 percent of the MTBE after 10 weeks; after 180 days, toluene was added, and 100 percent of the toluene was removed after 48 hours, while there was a drop in MTBE removal efficiency
- Pruden and others (2001) created five laboratory bioreactors seeded with liquor from municipal sewage that biotransformed 99.9 percent of the MTBE
- Vainberg and others (2002) studied a laboratory-scale granular activated carbon (GAC) fluidized bed bioreactor (FBR) seeded with a mixed MTBE-degrading culture and BTEX (removal rates are reported in the text)
- Stringfellow and Oh (2002) conducted a field bioreactor study in which MTBE degradation never occurred, yet in a second bioreactor, "spontaneous MTBE degradation began immediately"
- Wilson and others (2001 a) created a continuously stirred tank reactor (CSTR) seeded with mixed liquor from municipal sewage; no MTBE was removed in the control CSTR, although some MTBE was removed in the biologically active CSTR
- Wilson and others (2002a) concluded that TBA was rate-limiting in a biologically active CSTR with added MTBE and TBA

## Aerobic biodegradation by pure cultures

A summary of aerobic biodegradation of MTBE by pure cultures follows:

- Mo and others (1995) isolated 15 bacterial strains from sludge that degraded as much as 40 percent of 200 mg/l MTBE in two weeks of incubation
- Hanson and others (1999) culled the bacterial strain PM1 from a compost biofilter consortium and successfully degraded MTBE; "The overall biomass yield that was estimated from protein production at several MTBE concentrations was 0.18 mg cells/mg MTBE"
- Salanitro and others (2001) isolated species from the MC-100 consortium and studied effects on MTBE biodegradation
- Hatzinger and others (2001), using *Hydrogenophaga flava* ENV 735, demonstrated that MTBE and TBA degradation were dependent on two different enzymes
- Piveteau and others (2003) found that the strain CIP I-2052 could degrade TBA but not MTBE
- Francois and others (2002) determined that the mycobacterium *Austrofricanum* IFP 2012 could degrade 300 mg/l MTBE after 30 days of incubation; 68.7 percent of the MTBE was mineralized

## Cometabolism by alkane oxidizers

This cometabolic strategy relies on using alkanes as growth substrates. "There are several reports of cometabolic degradation of MTBE in fungi and bacteria. The degradative ability centers on the use of alkanes as growth substrates" (Fiorenza and Rifai, 2003). Summaries of cometabolic studies follow:

- Hardison and others (1997) used a filamentous fungus in a potato-dextrose broth to degrade diethyl ether, but not MTBE
- Steffan and others (1997) identified a monooxygenase enzyme from propane-oxidizing bacteria that degraded MTBE, ETBE and TAME
- Envirogen patented "the use of propane addition to stimulate MTBE biodegradation by either added propane oxidizers or by indigenous microorganisms" (Fiorenza and Rifai, 2003)
- Garnier and others (1999) isolated bacteria from a pentane soil enrichment and this "isolate degraded MTBE in the presence of pentane and did not degrade MTBE in the absence of pentane" (Fiorenza and Rifai, 2003)
- Hyman and others (1998) used a *Xanthobacter* strain and *Mycobacterium vaccae* in MTBE degradation studies; MTBE degradation was inhibited by acetylene but not by ethylene
- Chavaux and others (2001) found that *Rhodococcus ruber* and *Gordonia terrae* were able to degrade ETBE but not MTBE or TAME
- Lui and others (2001) observed the cometabolic degradation of MTBE by *Arthrobacter* when grown on butane

## MTBE biodegradation in mixtures

The most common contaminants that occur with MTBE are gasoline's BTEX components. Thus, most mixtures of MTBE will involve BTEX. Summaries of some studies reported in Fiorenza and Rifai (2003) follow:

- Chang and others (1993) "found the two *Pseudomonas* species (B1 and X1) isolated from a fluidized bed reactor treating BTX-contaminated groundwater; each used different constituents as sole carbon and energy sources and showed that different pairs of the substrates had different forms of interaction,

ranging from competitive inhibition to cometabolism"; researchers found a similar range of interactions while investigating MTBE biodegradation in the presence of BTEX

- Jensen and Arvin (1990) found that 40 mg/l MTBE had no effect on the degradation of benzene, toluene, ethylbenzene, o/m xylene, and naphthalene; 200 mg/l MTBE had a slight inhibitory effect on degradation
- Horan and Brown (1995) indicated that 740 mg/l of MTBE inhibited the mineralization potential of hexadecane by 50 percent
- Park and Cowan (1997) reported in Fiorenza and Rifai (2003) "that MTBE had only a slight effect on toluene biodegradation in *Pseudomonas putida* F1, but it almost doubled the times associated with oxygen uptake during benzene plus MTBE biodegradation... Researchers suggested that MTBE inhibited benzene biodegradation, but an alternative explanation is that the cultures were oxygen limited"
- Salanitro and others (2003) found that degradation rate of BTEX compounds present at 2 to 2.5 mg/l was not affected by 5 to 90 mg/l MTBE
- Fujiwara and others (1996) determined that 12.5 percent MTBE in gasoline did not affect gasoline degradation
- DaSilva and Alvarez (2002) saw no impact on BTEX biodegradation by 25 mg/l MTBE
- Ruiz-Aguilar and others (2002) observed "no decrease in BTEX biodegradation in aquifer microcosms from four different sites with different exposure histories under either aerobic, denitrifying or sulfate-reducing conditions in the presence of 10 mg/l MTBE" (Fiorenza and Rifai, 2003)

- Kane and others (2001) found benzene biodegradation was not affected by MTBE biodegradation in MTBE microcosms of aquifer material from two gasoline- and MTBE-contaminated sites
- Mo and others (1995) observed that "tert-butanol, butylformate, isopropanol, acetone and pyruvate reduced MTBE biodegradation in seven strains" (Fiorenza and Rifai, 2003)

Fiorenza and Rifai give many other examples, too many to be summarized in this article. When both BTEX and MTBE were present in biodegradative studies, researchers found the following:

- no effect on MTBE's or BTEX's degradation
- apparent simultaneous degradation
- sequential utilization of either MTBE or BTEX, depending on the microorganism PM1's growth substrate (when PM1 was involved)
- apparent inhibition of MTBE degradation
- lack of effect on MTBE degradation, yet inhibition of TBA degradation
- reduced rate of MTBE degradation
- enhancement of MTBE degradation

Fiorenza and Rifai (2003) also conclude that "It is impossible to generalize about MTBE biodegradation in the presence of co-contaminants, given that studies of mixed cultures and pure cultures show a variety of responses. What is probably most important is to understand how the co-contaminants affect one another at the site under investigation. While more kinetic studies are needed with pure cultures of MTBE degraders to ascertain the interactions among contaminant mixtures and provide insight into degradation pathways, it is likely that there will continue to be a range of interactions observed depending on the co-contaminants tested and the microbial species involved."

### Laboratory biodegradation studies

Results of MTBE anaerobic studies (the core of a BTEX plume is anaerobic) are mixed, indicating no degradation (recalcitrance) to significant degradation depending on environmental conditions. Conditions studied include soil type (silty, clayey, loamy), incubation under iron-reducing conditions, presence of alkylbenzenes, iron oxides, humic substances, nitrates, manganese, and sulfate. Fiorenza and Rifai (2003) contend that "It is now clearly established that MTBE degrades aerobically, by both mixed and pure cultures, to CO<sub>2</sub> and biomass. In general, slow growth has been observed, but organisms are now being isolated that appear to be quite well adapted to growth on MTBE."

Bioreactors can remove significant amounts of MTBE, and usually mixed cultures perform better than unmixed. Fiorenza and Rifai (2003) cite some important, unanswered questions:

- "Why is there low cell yield among some organisms? Is a cofactor/nutrient or electron acceptor missing?"
- What enzymes control the key steps in MTBE aerobic biodegradation? How does this vary among the known MTBE degraders?
- What cofactors might be limiting MTBE/TBA/HIBA degradation?
- What are the inducers and inhibitors of key enzymes in the MTBE biodegradation pathway, and what is the implication for remediation of mixed contaminant plumes?
- What is the anaerobic pathway for MTBE degradation, and what enzymes and cofactors are involved?
- Can the use of some recently developed tools for identification of microbial community structure provide insight into the presence or absence of MTBE biotransformation?"

Fiorenza and Rifai (2003) also discussed MTBE field studies, in-situ bioremediation and phytoremediation. These topics will be the subject of a future *UTTU* article.

### Reference

Fiorenza, S. and H.S. Rifai, "Review of MTBE Biodegradation and Bioremediation," *Bioremediation Journal*, Vol. 7, No. 1, 2003; <http://www.sciencedirect.com/science/journal/10889868>

*UTTU thanks Dr. Stephanie Fiorenza, Stephanie.Fiorenza@bp.com, for her help on this article.*



### UST testing, part II

By John Hartmann

The first part of this article (in *UTTU* Vol. 17, No. 5, 2003) introduced tank testing and described some tests normally performed on USTs. The second part describes tank deflection, tank-hole liners, detectors, indicators, monitors, overflow protection devices, precision testing and the significance of temperature changes.

### Measurement of tank deflection

Roundness is important in all tanks. An out-of-round, or deflected tank is flattened out somewhat and appears from an end view to be oval. Deflection measurements are used to determine whether a tank has lost its roundness.

Underground tanks derive some of their structural support from the surrounding soil. Excessive deflection causes stress in tank shells. By shortening the diameter between the top of the tank and the bottom, excessive deflection can also cause the suction tube or submerged pump inside the tank to penetrate the bottom.

*How and when deflection measurements are made.*

After an FRP tank has been delivered to the job site, but before it is installed, insert a tank gauge stick through an opening in the top of the tank. Hold the stick in a vertical position and note the reading, in inches, to measure the tank's diameter.

Later, after the tank has been installed in the excavation and backfill has been brought to the top of the tank, take a second deflection measurement. Compare the second reading with the first, and calculate any difference.

*Allowable deflection.* Slight tank deflection is tolerable, but deflection that exceeds maximums established by manufacturers may be a sign of structural damage. Maximum deflection ranges, worked out by FRP tank manufacturers, appear in the table below. (Be sure to check for specific maximum allowable deflection, which should be shown on the tank itself.)

Tank diameter (nominal)	Maximum allowable deflection
6 feet	5/8 inch
8 feet	1 1/4 inch
10 feet	1 1/2 inch
12 feet	1 1/2 inch

Notify the tank manufacturer immediately if these maximum deflection figures are exceeded at any time, and do not proceed with the project until the manufacturer has responded. FRP manufacturers will not honor a warranty on a tank that has not been installed in conformity with the manufacturer's specifications.

### Impervious tank-hole liners

Carefully inspect any impervious liner used in a tank excavation to ensure that the liner has not been damaged. Inspect the liner after it has been installed in the hole, but before any backfill has been added or any tanks

placed in the hole. Pay special attention to the seams on the liner. Manufacturers of impervious tank-hole liners provide instructions for testing and inspecting their products. The instructions also include procedures to follow when making last-minute repairs to the liners.

### Line-leak detectors

Pressurized systems with pumps located at the tank rather than at the dispenser are equipped with devices designed to detect leaks in the product lines between tanks and dispensers. These devices, called line-leak detectors, remain open unless the pressure drops (as it would if a leak developed in the line). A drop in pressure causes a spring-loaded poppet in the detector to partially close. The activation of this device either severely restricts or shuts off the flow in the line, signaling the operator that a problem exists. More sophisticated line-leak detectors will also actuate an alarm. Direct installers to make sure the detectors are operating properly before they close the excavation. Manufacturers' instructions that accompany line-leak detectors explain how to conduct installation tests.

Federal regulations require line-leak detectors to be capable of detecting a leak of three gallons per hour. A leak of this magnitude must be detected within one hour at a system pressure of 10 pounds per square inch.

API/RP1635 states that the correct functioning of various pieces of equipment should be checked before placing a new tank system in operation. Specifically, this recommended practice says installers should operationally test all other equipment (in addition to tanks and piping), including impact (shear) valves, and leak detector alarms.

### Line leak indicators

Suction systems require less-sophisticated leak detection systems. If prime is lost, then there is a leak. Use only one check valve in a suction system immediately under

the suction pump. Additional check valves can disguise the loss of prime or other symptoms of line leaks.

### In-tank electronic monitors

Electronic tank monitoring systems are becoming increasingly popular. These devices operate on the capacitance principle. In its simplest form, a capacitor works like this: take two metal plates (one negatively charged, the other positively charged) and position them parallel to each other. Any materials placed between the two plates will obstruct the flow of electricity between them. Some materials will resist the flow of electricity more than others. The flow rate of electricity through gasoline, for example, is not the same as the flow rate through water. If there is no material between the plates, a different flow rate is induced. The capacitor measures the dielectric (a material's capacity for resisting electric flow) between the two plates.

*Concentric capacitors.* One of the most widely used in-tank monitors is the concentric capacitor. The probe installed in the tank is an aluminum tube. Inside the aluminum tube is a glass tube. Electronic impulses flowing between the wires inside the glass tube and the outside aluminum tube measure the dielectric value of the product in between. A layer of water in the bottom of the tank will produce a different impulse rate from the gasoline above. To add to their technical sophistication, these probes are equipped with thermistors positioned along the sides of the aluminum tube, so the readings are temperature-compensated.

In leak-detection mode, these devices can measure liquid-level changes in a storage tank as small as 1/1,000 of an inch, or 0.1 gallon per hour. A leak-detection test in which a concentric capacitor is used requires 3-5 hours to complete.

*Magnetostrictive monitors.* The magnetostrictive monitor is a somewhat different type of in-tank monitor. Its

sensor is an aluminum tube containing a flat wire that is installed vertically in the tank. Outside the tube is a float ring with magnets inside. The float ring moves up and down the probe in response to the liquid level in the tank. Pulses moving through the magnets in the float ring cause the wire inside the tube to twist slightly. The system then measures the length of time it takes for the pulse to return from the point at which the twisting motion occurred.

Magnetostrictive probes can monitor difficult liquids, such as oxygenated fuels. But any water present in a tank of gasoline will drop to the bottom. In oxygenated fuels containing alcohol, water is difficult to identify because it mixes with the alcohol.

These in-tank electronic monitoring systems are highly sensitive instruments. Their accuracy should be verified after installation but before the tank system is paved over. Manufacturers' instructions include procedures for testing the accurate operation of the systems.

### Overfill protection devices

In-tank systems designed to slow, then cut off, the flow of product being delivered to a tank are commonplace. The simplest type of overfill protection device is a ball float valve installed below the open end of the tank vent line. As the liquid level in the tank rises, the ball moves up and begins to obstruct the open end of the vent line. This, in turn, reduces the flow of displaced vapor from inside the tank and prompts a reduction in the flow rate on the delivery hose.

A more sophisticated overfill protection device consists of a valve located inside a tube installed vertically in the tank's fill pipe. A float mechanism, positioned either outside or inside the tube, actuates the valve. As the level of liquid rises, the float mechanism closes the valve. This type of overfill protection device needs to be calibrated to conform with the tank capacity. Check manufacturers' instructions for calibration procedures.

### Precision test

The section called "Final Testing" in API/RP1635, *Management of Underground Storage Systems at Marketing and Distribution Facilities*, recommends that the precision testing of tanks and piping be administered after paving but before the system is put into operation. Other recommended practices have similar recommendations or requirements.

What is a precision test? *NFPA 329, Underground Leakage of Flammable and Combustible Liquids*, originally defined a precision test as "any test that takes into consideration the temperature coefficient of expansion of the product being tested as related to any temperature change during the test, together with other variables, and is capable of detecting a loss of 0.05 gal (190 ml) per hour."

Although the term "precision test" still appears in various industry recommended practices, the 1993 edition of NFPA 329 has replaced this term with "tank tightness test." The testing criteria established in the 1993 edition of NFPA 329 conform to those of the U.S. EPA Office of Underground Storage Tanks. To qualify as a tank tightness test, within the meaning of NFPA 329, a testing procedure must be capable of detecting a leak as small as 0.1 gallon per hour at least 95 percent of the time. Under the new NFPA 329 definition, approved systems used for testing the tightness of underground tanks must demonstrate a probability of false alarms of no more than 5 percent.

To qualify, tank tightness testing systems must be evaluated by an independent third-party testing laboratory. Laboratories are required to test the systems in accordance with criteria developed by the U.S. EPA. The report of the third-party laboratory will serve as evidence that the system is capable of performing within the required accuracy limits when operated by a trained individual.

### Significance of temperature

If the product in a 6,000-gallon tank increases in temperature by 0.03° F, the volume of liquid will increase by 0.108 gallons. Such a volume increase seems trivial, except that federal regulations define a leak as a release in which 0.1 gallon or more escapes from the tank in the course of an hour.

This means that a leak of 0.1 gallon per hour might go undetected if, during the same hour in which the leak rate was measured, the temperature in the tank increased slightly, because the extra liquid volume created by temperature-induced expansion might exceed the 0.1 gallon of liquid that escaped from the tank during the same period.

### Difficulty of stabilizing tank temperature

Contrary to what was once believed, filling a tank with gasoline 10 or 12 hours before running a leak test does not generally stabilize the temperature of the product in the tank. After several days, a tank of gasoline may stabilize to ground temperature; however, even the ground temperature can fluctuate by 0.02 to 0.25° F per hour.

Another influence on product temperature is temperature stratification (sometimes called layering), which results when new product at one temperature is added to product already in the tank at a different temperature. Layering can also be caused by difference in ground temperature at different depths. The ambient (outside) temperature during the period in which the tank-system tests are being run can also affect test results. Extreme hot or cold temperatures may make it impossible to use some types of precision testing equipment successfully. In extremely cold weather, temporary shelters may be necessary to house test equipment and warm it with space heaters.

The third and last section of this article will describe testing in cold weather, tank deflections, other variables, post-installation testing, precision testing, documentation and test planning.

## Reference

Hartmann, John, "Testing," in *Underground and Above-ground Storage Tank Inspection*, Section 5, April 21 – 23, 2003, Ft. Gordon, Georgia, given by the University of Wisconsin-Madison, <http://epdweb.engr.wisc.edu>

API, American Petroleum Institute, <http://api-ep.api.org>, 202-682-8000

NFPA, National Fire Protection Association, <http://www.nfpa.org>, 617-770-3000

UTTU thanks John Hartmann, [jhartmann@pe-t.com](mailto:jhartmann@pe-t.com), publisher of *Petroleum Equipment & Technology Magazine Archive* (<http://www.pe-t.com/>) for allowing us to reprint this article. John Hartmann & Associates may also be reached at 847-382-4010.



## Research notes

### An Environmentally Friendly Decontamination Protocol for Ground Water Sampling Devices

Parker, L.V. and T.A. Ranney, *Ground Water Monitoring & Remediation*, Vol. 23, No. 2, Spring 2003, <http://www.ngwa.org>

Parker and Ranney (2003) tested the ability of several decontamination protocols to remove residual contamination from materials typically found in groundwater sampling devices. Contaminants tested included volatile organic compounds (VOCs), pesticides and explosives. They found that organic materials could be readily removed from nonpermeable, stainless steel surfaces by

using a simple detergent wash and distilled water rinse of unheated water. Permeable polymeric materials do not undergo decontamination as successfully, and this is a function of

- the substance's porous or sorptive nature
- contact time
- physical characteristics of the organic contaminants such as its aqueous solubility, volatility, and propensity to adsorb onto/absorb into materials

Sampling devices tested included

- a bailer made of fluorinated ethylenepropylene (FEP)
- top and bottom check assemblies made of PTFE (polytetrafluoroethylene)
- bladder pumps made of stainless steel body and PTFE bladder
- twinline bonded tubing

Researchers developed protocols for decontaminating the bailer and the bladder pump, which are described in the text of their paper. From this study, researchers observed:

- if groundwater sampling devices are not decontaminated, residual contamination can be carried over into the next sample
- cleaning with a hot-water detergent wash, hot-water rinse, and DI-water rinse followed by hot-air drying effectively removed TCE from a bailer and bladder pump but not from the tubing
- briefly rinsing with organic solvents did not aid in VOC removal
- VOCs were readily removed from the less sorptive PVC test pieces by washing with a hot detergent solution and rinsing with hot water

- if the material were a more sorptive PTFE, additional oven drying was necessary (oven drying speeds diffusion of chemicals)
- "a considerably cumbersome, expensive and hazardous step (i.e., solvent rinsing) could be eliminated from decontamination protocols without jeopardizing removal efficiency"

Researchers recommend devoting future efforts to cleaning the tubing outside and refining the hot-air cleaning method. "Additional research could produce a method that is applicable to a variety of types of sampling devices and environments."

### Bacterial Production Stimulated Across the Zone of Influence of a Ground Water Circulation Well in a BTEX-Contaminated Aquifer

Montgomery, M.T., Spargo, B.J., Mueller, J.G., Coffin, R.B., Smith, D.C. and T.J. Boyd, *Ground Water Monitoring & Remediation*, Vol. 22, No. 3, Summer 2000; <http://www.ngwa.org/>

Researchers contend that it is "difficult to evaluate whether or not biodegradation per se has occurred in the field situations where contaminants can be attenuated through a variety of abiotic mechanisms (e.g., volatilization or dilution.)" In this study, researchers evaluated "the effectiveness of GCWs (groundwater circulation wells) at stimulating heterotrophic activity by comparing bacterial production as measured by rates of <sup>3</sup>H-leucine incorporation into protein. The accurate measurement of bacterial productivity is important for determining whether or not the bacterial assemblage has the metabolic carbon demand to account for biodegradation of the missing contaminant... In aquatic ecosystem studies, rates of incorporation of <sup>3</sup>H-thymidine into DNA

and  $^3\text{H}$ -leucine into protein are predominantly used to measure overall heterotrophic growth of the microbial assemblage."

Researchers studied a LUST site at Port Hueneme, California, being remediated with GCW technology. The technology consisted of a blower designed to generate negative pressure in the treatment well; water rises and air is drawn into a system leading to a stripping reactor. Remediators installed 12 groundwater monitoring wells, and an additional eight monitoring wells were installed around three smaller GCWs.

Bacterial abundance was determined using acridine orange staining and epifluorescence microscopy. Researchers used the  $^3\text{H}$ -leucine incorporation method to measure bacterial productivity.

The GCWs help stimulate production by

- increasing oxygen transfer to the subsurface
- circulating limiting nutrients
- enhancing bioavailability of hydrocarbons

Montgomery and others (2002) concluded that the GCW treatment system was able to remove about 62.6 kg/C/year. Furthermore, "Even if all the bacterial carbon demand was met using BTEX compounds, biodegradation could account for a maximum of 4.3 percent of the estimated abiotic removal of BTEX by operation of the GCW. In fact, a related study determined that mineralization rates of benzene and toluene were dramatically reduced within the GCW during operation of the treatment system. Although total heterotrophic production was clearly stimulated by operation of the GCW, the system appeared to have minimal impact on enhancing in-situ biodegradation under these environmental conditions."

### CPT-Hole Closure

Noce, T.E. and T.L. Holzer, *Ground Water Monitoring & Remediation*, Vol. 23, No. 1, Winter 2003;

<http://www.ngwa.org>

Holes created by cone penetration technology (CPT) can be 1.75 inches (4.4 cm) in diameter by 98.4 feet (30 m) long. Noce and Holzer (2003) found that these holes can be open for approximately three years in a clayey silt to a silty clay. In other lithologies, such as an estuarine clayey silt, closure was likely immediate. Authors caution users of CPT to beware because "Despite their small diameter, CPT holes may remain open for years—and possibly decades—and provide paths for rapid migration of contaminants."

### Evaluation of the Johnson and Ettinger Model for Prediction of Indoor Air Quality

Hers, I., Zapf-Gilje, R., Johnson, P.C. and L. Li, *Ground Water Monitoring & Remediation*, Vol. 23, No. 1, Winter 2003, <http://www.ngwa.org>

Researchers recently evaluated the Johnson and Ettinger (1991) model that predicts indoor air quality. The model is used for regulatory and guidance purposes in North America. Factors that affect vapor intrusion pathways include "biodegradation, chemical transformation, sorption, contaminant source depletion, chemical transformation, geologic heterogeneity, soil properties (moisture content, permeability, organic carbon content), building properties, meteorological conditions, and building ventilation rates."

Some conclusions from this study follow:

- the model "is moderately to highly sensitive to soil-gas advection rate into the building"
- "estimation of effective diffusion coefficient is subject to considerable uncertainty...[some of which] can

be reduced through better site characterization, including careful lithological descriptions, testing of moisture content, grain size distribution and water retention and appropriate consideration of the effect of surface barriers on soil moisture content"

- "only a limited number of high-quality and comprehensive field studies exist that can help validate models for the vapor intrusion pathway"

### LUST Cleanup Landscape Changing: Landfilling Still In, Pump-and-Treat on the Way Out

Kostecki, P. and M. Nascarella, *Contaminated Soil Sediment and Water*, January/February 2003;

<http://aehsmag.com>

Scientists from the University of Massachusetts compared the techniques used to remediate LUSTs in 1985 and 2001. In 1985, of the 50 states surveyed:

- 72 percent used landfilling
- 58 percent used landfarming
- 26 percent used bioremediation (known as in-situ biodegradation and microbial degradation) on a trial basis

In 2001, of the 35 states surveyed, technique usage was as follows:

- 31 percent, landfilling
- 19 percent, MNA (monitored natural attenuation) for soil, 67 percent for groundwater
- 18 percent, soil vapor extraction
- 16 percent, low-temperature thermal desorption
- 9 percent, landfarming
- 3 percent, biopiles
- 2 percent, incineration
- 2 percent, bioventing

- 12 percent, pump-and-treat
- 9 percent, in-situ bioremediation
- 9 percent, air sparging
- 3 percent, biosparging

Authors also report: "While RBCA (risk-based corrective action) appears to have some modest influence on the remediation selection (24 of 35 states reported this), the presence of MTBE does not appear to be impacting remediation selection as prominently." Because of MTBE's mobility and the pressure to remediate, more states may consider MNA, a lengthy procedure, an unviable option.

Kostecki and Nascarella (2003) state that "The most interesting result of the 2001 survey may be that no new technology has been developed to remediate contaminated soils and groundwater in the last decade."

### Monitoring Partitioning Tracer Testing and Surfactant Flooding by In-Line Gas Chromatography Techniques

Silva, J.A.K., Mariner, P.E., Meinardus, H.W. and J.S. Ginn, *Ground Water Monitoring & Remediation*, Vol. 23, No. 1, Winter 2003, pgs. 85-92; <http://www.ngwa.org>

Researchers developed an automated in-line analytical system "to provide near real-time results for partitioning interwell tracer testing (PITT) and surfactant-enhanced aquifer remediation (SEAR)." The system is compact, mobile and easy to use. It consists of an in-line GC apparatus, and custom-made components "linked electronically to automate sample retrieval and delivery."

The PITT "involves the subsurface injection and subsequent extraction of a suite of partitioning and non-partitioning tracers within an engineered interwell flow field. In the presence of residual NAPL contamination, these tracers chromatographically separate. Monitoring tracer

concentrations in the produced well effluent provide elution profiles that are further used to estimate the volume of residual NAPL present within the aquifer volume swept by these tracers."

Advantages of their innovative system includes:

- elimination of containerizing, shipping and storing samples
- minimization of sample exposure to air
- generation of PITT and SEAR data on-site and in near-real time
- reduction of unit sample analytical cost by as much as 85 percent, based on a commercial laboratory cost of \$85 per sample

### Retention and Transport of a Hydrocarbon in a Silt

Cui, Y.J., Delage, P. and P. Alzoghbi, *Geotechnique*, Vol. 53, No. 1, February 2003; <http://www.thomastelford.com/jol/>

Scientists investigated the retention and transport properties of a light hydrocarbon in a silt. The goal was to define "parameters of NAPL retention and transport in a silt compacted at various densities and water contents." The cell used in this research is one normally used for determining unsaturated oil permeability. In addition, researchers used mercury intrusion porosimetry to study the microstructure of intact and polluted silt samples.

Their research showed that "the oil retention and transport properties were significantly dependent on the density and water content of the polluted soil. Looser samples have larger macropores that are full of air if the water content is low. Samples appeared sensitive to the application of a small value of suction (25 kpa) that expelled a significant amount of oil. Such soils would probably be remediated by an easier decontamination, in particular, using air venting techniques."

### Other papers of interest include the following:

"A Simple Model of Soil-Gas Concentrations Sparged into an Unlined Unsaturated Zone," Ostendorf, D.W., Hinlein, E.S., Lutenegger, A.L and P.S. Tehrany, *Ground Water Monitoring & Remediation*, Vol. 23, No. 2, Spring, 2003, pgs. 73-83; <http://www.ngwa.org>

"Analytical Solutions for Free-Hydrocarbon Recovery Using Skimmer and Dual-Pump Wells," Johns, R.T., Lake, L.W., Obigbesan, A.B., Bermudez, L., Hassan, M.R. and R.J. Charbeneau, *Ground Water Monitoring & Remediation*, Vol. 23, No. 1, Winter 2003; <http://www.ngwa.org>

"Bioindicators: Essential Tools for Realistic Site Assessment and Remediation Cost Control," E.J. Sillioux and J.R. Newman, *Soil, Sediment & Water*, March/April 2003; <http://aehsomag.com>

"Bioremediation in Bedrock: Using Bioremediation to Treat Dissolved BTEX and MTBE in Fractured Bedrock," D. Laughlin, *Soil, Sediment & Water*, March/April 2003; <http://aehsomag.com>.

"Co-Occurrence of MTBE and Benzene, Toluene, Ethylbenzene, and Xylene Compounds at Marinas in Large Reservoir," An, Y.J., Kampbell, D.H. and M.K. Cook, *Journal of Environmental Engineering*, September 2002; <http://ojps.aip.org/eoo>

"Effects of pH, Moisture and Flow Pattern on Trickle-bed Air Biofilter Performance for BTEX Removal," Lu, C., Lin, M.R. and C. Chu, *Advances in Environmental Research*, Vol. 6, No. 2, March 2002; <http://www.elsevier.com>

"Effects of Singapore Soil Type on Bioavailability of Nutrients in Soil Bioremediation," *Advances in Environmental Research*, September 2002 (available online); <http://www.elsevier.com>

"Environment vs. Bacteria or Let's Play 'Name That Bacteria'," Nyer, E.K., Payne, F. and S. Sutherson, *Ground Water Monitoring & Remediation*, Vol. 23, No. 1, Winter 2003; <http://www.ngwa.org>

"Experimental Investigation of Contaminant Transport in Coastal Groundwater," Zang, Q., Volker, R.E. and D.A. Lockington, *Advances in Environmental Research*, Vol. 6, No. 3, September 2002; <http://www.elsevier.com>

"Importance of Nonequilibrium Sorption Conditions: Contaminated Soil," Opdyke, D.R. and R.C. Loehr, *Ground Water Monitoring & Remediation*, Vol. 22, No. 3, Summer 2002; <http://www.ngwa.org>

"Initiation of MTBE Biotreatment in Fluidized-Bed Bioreactors," Stringfellow, W.T. and K.C. Oh, *Journal of Environmental Engineering*, September 2002; <http://ojsps.aip.org/eeo>

"Monitoring Oxidation of Chlorinated Ethenes by Permanganate in Groundwater Using Stable Isotopes: Laboratory and Field Studies," Hunkeler, D., Aravena, R., Parker, B.L., Cherry, J.A. and X. Diao, *Environmental Science and Technology*, Vol. 37, No. 4, 2003; <http://www.pubs.acs.org>

"Use of Membrane Bioreactor for Biodegradation of MTBE in Contaminated Water," Morrison, J.R., Sudian, M.T. and A.D. Venosa, *Journal of Environmental Engineering*, September 2002; <http://ojsps.aip.org/eeo>

"Vacuum Extraction-Based Response Equipment for Recovery of Fresh Fuel Spills from Soil," Halmemies, S., Grondahl, S., Arffman, M., Nenonen, K. and T. Tuhanen, *Journal of Hazardous Materials*, Vol. 97, February 2003, pgs. 127-143; <http://www.elsevier.com>



## Information sources

### U.S. EPA publications and information

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

- Abstracts of Remediation Case Studies, Vol. 7 (EPA 542-R-03-011)
- Surfactant-Enhanced Aquifer Remediation (SEAR) Implementation Manual (TR-2219-ENV)
- Technology News and Trends; articles in the past have included Biobarrier Treats Mixed MTBE Plume at Port Hueneme, Phytoremediation Field Studies Underway for MTBE Removal, and Accelerated BTEX/MTBE Destruction Achieved through Chemical Oxidation

### Other EPA publications

Directory of Technical Assistance for Land Revitalization (EPA 542-B-03-001), [http://www.brownfieldstsc.org/publications\\_index.htm](http://www.brownfieldstsc.org/publications_index.htm)

Cleaning up Contaminated Properties for Reuse and Revitalization: Effective Technical Approaches and Tools Conference—After Action Information; <http://www.brownfieldstsc.org/revtech/index.html>

Compendium of Federal Facilities Cleanup Management Information (EPA-505-B-03-002), <http://epa.gov/swerffrr/documents/ffcc.htm>

Environmental Technology Verification Report: Groundwater Sampling Technologies Geoprobe Inc. Mechanical Bladder Pump, Model MP470 (EPA 600-R-03-086), <http://www.epa.gov/etv/pdfs/vrvs/> (select geoprobe)

Oil Spill Program Update, <http://www.epa.gov/oilspill/pdfs/O703update.pdf>

REACHIT, Remediation and Characterization Innovative Technologies database, <http://www.epareachit.org>

Using the Triad Approach to Streamline Brownfield Site Assessment and Clean Up Brownfields, Technology Primer Series (EPA 542-B03-002), [http://www.brownfieldstsc.org/publications\\_index.htm](http://www.brownfieldstsc.org/publications_index.htm)

### Other documents and Web sites

Automated Groundwater Flow System for Contaminant Fate and Transport Analyses, [http://www.crrel.usace.army.mil/erd/ground\\_water.html](http://www.crrel.usace.army.mil/erd/ground_water.html)

Environmental Cleanup at Navy Facilities: Adaptive Site Management, <http://www.nap.edu/catalog/10599.html>

ITRC Quarterly Update, <http://www.itrcweb.org/ITRC0903Update.pdf>

**UTTU obtained many of these sites from TechDirect (<http://clu-in.com/techdrect>) and Ground Water Monitoring and Remediation (<http://www.ngwa.org>). UTTU thanks the editors and writers for allowing us to reprint this material.**