

# Underground Tank Technology Update

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## MTBE biodegradation and BC-1

This article summarizes some current ideas and studies concerning MTBE biodegradation. It also describes an MTBE-degrading consortium (BC-1), which could possibly be used to seed a contaminated aquifer (*Salanitro and others, 1998*).

### The BC-1 consortium

Shell Oil created the BC-1 consortium whose characteristics are listed in Table 1.

The BC-1 consortium contains about five to six species of gram-positive and gram-negative microbes from chemically treated biosludge. BTEX degradation is low in this culture.

### Suggested MTBE biodegradation pathways

Research on MTBE shows the following:

- MTBE, when biodegraded, may be oxidized to a short-term intermediate, t-butyl formate (TBF)
- TBF undergoes hydrolysis and/or very rapid microbial breakdown by the consortium BC-1
- Graphium, a fungus, can also biodegrade MTBE to TBF
- petrochemical refinery biosludge enrichments have

facilitated aerobic oxidation of MTBE; although they don't know why, researchers have found that enzymatic systems that degrade hydrocarbons can oxidize ether

- methane-oxidizing and ammonia-oxidizing bacteria have oxidized alkyl ethers such as dimethyl and diethyl
- a monooxygenase-type activity, presumed to occur in the initial oxidative cleavage to MTBE, forms formaldehyde and t-butyl alcohol (TBA)
- an anaerobic river sediment enrichment was shown to transform MTBE to TBA
- MTBE (72 mg/L) had no effect on methanogenesis from glucose
- propane-oxidizing microbes isolated from soil can oxidize MTBE to TBA and metabolize TBA to 2-methyl-3-hydroxypropane and then to 2-hydroxyisobutyrate; these latter steps may be rate-limiting
- ether-degrading cultures grow poorly on TBA
- BC-1 can break down MTBE to acetate
- researchers have developed other bacterial consortiums; Shell has developed consortiums up to BC-4

### Other MTBE studies

Researchers observed ether biodegradation in a continuous cell recycle chemostat or porous pot-type reactor. After several weeks of adaptation, effluent removals exceeded 99 percent. In the reactor, MTBE was the sole carbon source (100-200 mg/L) while biosolids (1-5 g/L) were retained with minimal loss to the effluent. The electron acceptor was oxygen.

Feature	Characteristic
Microbial composition	Mixed bacteria (gram-positive and gram-negative) pure cultures, hydrocarbon oxidizers
Maintenance	Continuous cell recycle reactor
Metabolism	Strictly aerobic
Proposed pathway	MTBE → TBE → IPA → DMK <sup>1</sup> → Pyruvate → Acetate → CO <sub>2</sub>
Metabolites detected	Uncommon in sludges, soils and groundwater
Ethers degraded	MTBE, ETBE, TAME, DIPE, DEE, MBE <sup>2</sup>
Growth rate	Low (≤ 0.05/d)
Apparent cell yield	0.1 - 0.2 g/cells MTBE
Stoichiometry	C <sub>5</sub> H <sub>12</sub> O + 6.5 O <sub>2</sub> + 2 HN <sub>3</sub> → 0.2 C <sub>5</sub> H <sub>7</sub> NO <sub>2</sub> + CO + 5.6 H <sub>2</sub> O
Substrate inhibition	Decrease in removal rate with increase in concentration
Factors affecting growth/activity	Temperature < 20°C; pH < 6; DO < 1 mg/L; high loading (BOD, MTBE)
Water biotreating	Suspended solids, fixed-film, fluidized bed reactors; longer hydraulic and biomass detention times
MTBE effects on BTEX	Little or none (90 mg/L)
Indigenous ether-degraders (natural attenuation rate)	Uncommon or very slow adaptation/growth, ≥ 3 to 5 times slower than BTEX (0.001/d)
In-situ aquifer bioaugmentation	Lab findings (soil/groundwater microcosm inoculation)

<sup>1</sup> Methyl tert butyl alcohol, t-butyl alcohol, isophthalic acid, dimethyl ketone

<sup>2</sup> Methyl tert butyl alcohol, ethyl-tert butyl alcohol, 1,1,1-tris aminomethyl ethane, diisopropyl ether, diethyl ether, methyl butyl ether

Table 1. Properties of the MTBE-degrading culture, BC-1 (from *Salanitro and others, 1998*).

Other studies are trying to understand why MTBE is a poor growth substrate for activated sludge and soil microbes. "High-energy-yielding substrates such as propane and glucose (> 9 Kcal/g-C) produce higher cell yields (> 1 g cell dry wt./g-carbon) while highly oxidized, low-energy-containing compounds (e.g. formate and oxalate) support low cell growth (< 0.5g/g-C). MTBE, like most TAME, ETBE and DIPE, contains about 12 Kcal energy/g-C, but cell yields are low (0.1-0.3g/g-C) with enrichment cultures utilizing the ether as sole source of carbon." Bioenergetics suggest that ether somehow interferes with the cell's ability to produce ATP.

Researchers also learned that

- the proposed stoichiometry for MTBE biodegradation indicates that oxygen demand requirements for the growth of ether-degrading cultures on MTBE are about 2 to 2.5 mg O<sub>2</sub>/mg MTBE vs. benzene which is about 3.1 mg O<sub>2</sub>/mg MTBE
- MTBE inhibits its own degradation in BC-1 at high concentrations
- removal rates (mg/g cells) decline with increasing MTBE levels with a significant rise in the Km saturation constant for ether
- why BC-1 or other adapted cultures can metabolize MTBE to CO<sub>2</sub>, yet obtain little energy for cell synthesis, is not clear; uncoupled growth with substrate utilization ("energy-spilling" metabolism) results in "apparent" high maintenance energy requirements and has been documented for pure cultures of bacteria growing under conditions in which yields are suboptimal
- preliminary evidence suggests that MTBE-cultured cells of BC-1 may be less capable of taking up Na<sup>+</sup> ions compared with the consortium grown to high yields on sucrose
- studies on biotreating MTBE in mixed wastes or groundwater indicated that MTBE is sensitive to the following conditions:
  - low temperature (< 20°C)
  - low pH (< pH 6)
  - hypoxic conditions (dissolved oxygen < 1 mg/L)
  - substrate (BOD or MTBE) loading ≥ 0.1 (F/M)
  - hydraulic and cell detention times; times ≥ 0.25-1 and ≥ 20-25 days, respectively, and a maximum loading of 10 mg produced maximum MTBE removal rates ≤ 100 µg/L effluent MTBE
- a field pilot-scale granular activated carbon fluidized bed (30 gal) reactor seeded with BC-1 could treat MTBE (1,000 µg/L) in groundwater down to 20 to 200 µg/L with volumetric flows of ≤ 3.5 gpm and a maximum loading of 10 to 40 mg/L reaction volume/day; data indicate it may be difficult to treat MTBE mass removals to very low µg/L levels in biotreatment systems with high flows and short biosolid times (< 20 days); there was no volatilization here—the volatilization rate was known prior to adding the culture

## BTEX and MTBE

Experiments conducted with MTBE and BTEX in aquifer soil and groundwater microcosms indicate the following:

- aromatic hydrocarbons (1-5 mg/L) degraded at varying rates (0.02 - 0.4/d) but were not significantly affected by ether levels of 5 to 90 mg/L
- intrinsic biodegradation may exist in some groundwater after a long period under aerobic, but not anaerobic, conditions
- high MTBE concentrations (> 30 mg/L) may increase the lag time slightly (7 to 14 days) before BTEX degradation begins
- high MTBE concentrations of 740 mg/L can inhibit (50 percent) the mineralization of <sup>14</sup>C-hexadecane to <sup>14</sup>CO<sub>2</sub>
- MTBE is not metabolized by BTEX-degrading organisms
- the presence of BTEX has no effect on ether degradation
- in a biotreating realm, however, MTBE would compete for O<sub>2</sub> if MTBE and BTEX were present in sufficient concentrations
- field-derived intrinsic attenuation rates for MTBE in sandy and clayey-sand aquifers were, respectively, 0.0012/d and 0.001/d based on several years of careful plume monitoring and modeling

Microbial removal efficiencies vary. For instance, biosludges from petrochemical plants and other contaminated subsoil and groundwater in bioassay systems with low-level (1-5 mg/L) MTBE and adequate O<sub>2</sub> have efficiencies varying from 0.01 to 1.2 mg/g cells/d (wastewater treatment plant biosludges) to 0.05 to 1.6 mg/L/d (groundwater). "Refinery sludges contain 1,000 times fewer degraders/g biomass and have at least 100 to 1,000 times lower MTBE removal rates than BC-1 . . . MTBE-degrader populations are also usually quite low to non-detect (100/L to 0/L) in groundwater or aquifer soils. Rates of removal by bioattenuation would be slower than the bulk groundwater velocities because of the low growth rates of indigenous or selected ether degraders."

## Soil microcosm studies

Salanitro and others observed intrinsic MTBE biodegradation in subsoil samples from a terminal and retail site where MTBE had been present for some time. Researchers found that BTEX (also present in the samples) degraded rapidly with a half-life less than 7 days in two of three samples. MTBE was completely metabolized in two samples after a lag period of 1 to 3 weeks to non-detectable levels (< 10 µg/L) within 3 to 4 weeks. Microcosm studies involving addition of BC-1 (20 to 50 mg/L) resulted in a rapid decline of MTBE with a half-life similar to BTEX.

Another contaminated site showed BTEX and MTBE half-lives, respectively, of < 7 and 21 days. Addition of 50 to 100 mg BC-1/Kg aquifer soil reduced the MTBE half-life to < 7 days. Another site containing TBA-contaminated soils was degraded by indigenous organisms with a half-life of 16 days. Addition of BC-1 reduced the half-life of TBA and the MTBE present to 3 to 5 days. *(Reviewer's note: such statements would be stronger if proof of a kinetic model was offered.)*

A saturated column flow-through using a medium grain sand containing MTBE (3 mg/L) and BC-1 showed maximum removal rates of 90 to 99 percent after 20 days, with effluent levels stabilizing at 0.1 to 0.3 mg/L. Little or no MTBE loss was observed in the control column. Researchers also found that most of the inoculant was retained in the seeded core, suggesting that "microbes inoculated into an aquifer soil would migrate only a short distance and also disperse/dilute into groundwater flow paths."

### Aquifer seeding

Salanitro and others (1998) describe scenarios such as pump-and-biotreat, natural attenuation, and microbial seeding that may be applicable to MTBE-contaminated groundwater. "Although such biotreaters can be inoculated with active ether-degrading cultures, the cost-effectiveness of consistently treating groundwater constituents (BTEX and MTBE) to very low concentrations ( $\leq 20 \mu\text{g/L}$ ) from diluter streams (low mg/L) at relatively high flow rates (10 to 30 gpm or higher) is not known for typical retail sites where underground gasoline tank releases have occurred. Other factors such as total loading (TPH organics), nutrient requirements for optimum biotreatment ( $\text{O}_2$  transfer,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ ) and the potential for  $\text{Fe}^{2+}$  oxidation fouling also need to be considered in optimizing this remediation technology" (Salanitro and others, 1998). Most researchers use mixed cultures or a consortia, although the specific genus—pure cultures—of rhodococcus and ruddivax have been used to treat MTBE-contaminated groundwater.

"Our survey results on the presence of ether-degraders in soil and groundwater show that these populations are too low and/or grow too slowly to effectively attenuate observed levels of MTBE in aquifer plumes. However, we have demonstrated that inoculation of subsoils and groundwater with ether-degrading microbes (20 to 200 mg cells/Kg aquifer material) can markedly shorten the half-life of the oxygenate." Success of the soil inoculants to stimulate degradation will depend on the following factors:

- survival
- decay and rate of growth
- adaptation
- substrate/energy utilization and availability
- microbial competition among existing heterotrophs

The effectiveness of an MTBE-degrading biobarrier will depend upon several factors:

- culture decay and dilution
- persistence
- heterotrophic competition
- long-term maintenance of metabolic activity in the soil matrix
- spacing between injection boreholes
- dispersion/dilution/transport of inoculant within and outside the biobarrier
- ability to transport  $\text{O}_2$  and sustain adequate dissolved  $\text{O}_2$  levels

### Reference

Salanitro, J.P., Chou, C.S., Wisniewski, H.L. and T.E. Vipond, "Perspectives on MTBE Biodegradation and the Potential for In-Situ Aquifer Bioremediation," 1998, paper presented at the *Southwestern Regional Conference of the National Ground Water Association*; 800-332-2104; <http://www.ngwa.org>.

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*UTTU thanks Dr. Joseph Salanitro, Equilon Enterprises, (jpsalanitro@shellus.com), for his help on this article.*



## Engineered in-situ MTBE biodegradation

Researchers conducted a field pilot test at Port Hueneme, California, to determine the efficiency of enhanced MTBE biodegradation, EMB. They wanted to develop a cost-effective technique that could control the leading edge of an MTBE plume or degrade the source; to degrade the source would require additional microbial concentration (*Salanitro and others, 1999*).

### Field test features

Features of the test included the following:

- a network of O<sub>2</sub> injection wells
- an in-situ biobarrier of MTBE-degraders, such as BC-4 culture (see the previous article)
- an array of monitoring wells upstream and downstream of the treatment zone

### Site description

In 1984-1985 several thousand gallons of leaded gasoline containing MTBE were released from USTs at the Naval Base in Port Hueneme. In 1997-1998, sample analysis of groundwater indicated the plume had traveled more than 4,000 feet from the source. The plume is at least 400 feet wide. About 75 percent of the soluble plume is solely MTBE. Most of the BTEX in the release attenuated near the source (within about 400 feet). Other characteristics of this site include

- a water table located about 10 feet below ground surface
- an upper aquifer with a thickness of 10 feet
- upper and lower portions of the aquifer that consist of silty loam and fine to medium sandy soils
- apparent groundwater velocity varying from 0.1 to 0.3 feet (upper) and 0.3 to 0.5 feet (lower)

### Field test plots

Researchers located the test site approximately midway down the advancing MTBE plume. Here, "MTBE is the only soluble fuel constituent, and it is present at concentrations varying from 2,000 to 8,000 µg/L. The DO levels in this area (within the first 400 feet) were < 1 mg/L prior to the test." The test plan consisted of 3 plots (Figure 1):

- O<sub>2</sub> + BC-4 seeded biobarrier
- O<sub>2</sub> only
- a control no-treatment zone

Each test plot was

- aligned parallel to the initial estimated groundwater flow directions
- 20 feet wide by 40 feet long
- spaced 10 feet from any other test plot

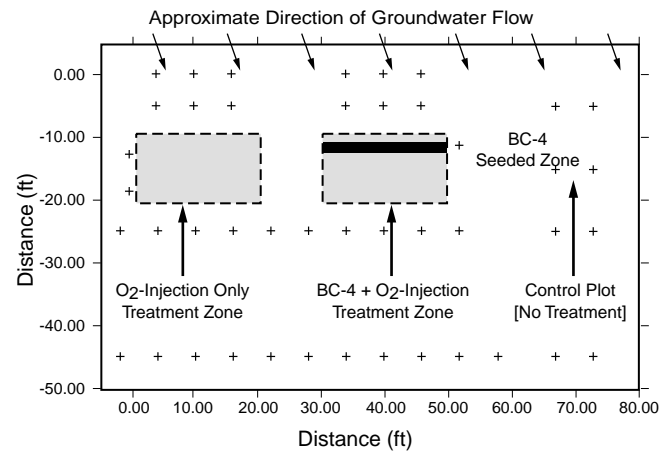


Figure 1. Field test site (from *Salanitro and others, 1999*).

The O<sub>2</sub> and BC-4 seeded biobarrier plot contained a treatment zone of a BC-4 inoculated area with an oxygen delivery system. The BC-4 microbial consortium

- had a concentration of 200 to 400 mg/L per kilogram of soil
- was grown with MTBE as the sole carbon source
- had an MTBE removal rate of 20-30 mg/g cells/hr
- was injected at points across and throughout the depth of the target treatment zone

The oxygen delivery system consisted of pure oxygen injection wells that were designed, placed and operated to optimize oxygen delivery efficiency while ensuring the necessary conditions for aerobic biodegradation of MTBE by BC-4 (DO > 2 mg/L).

The O<sub>2</sub> only plot consisted of only O<sub>2</sub>-injection and monitoring wells that were constructed, placed and operated in a manner similar to those used in the O<sub>2</sub> + BC-4 seeded plot.

The control plot was maintained as a "no treatment cell" and contained only monitoring wells.

Workers installed monitoring wells (1-inch PVC pipe) with a direct-push soil coring system and screened them over 5-foot intervals at 10 to 15 feet and 15 to 20 feet—designated as shallow and deep respectively. Workers took groundwater samples after purging one well volume and analyzed them for MTBE, tert-butyl alcohol and other MTBE degraders.

### Oxygen delivery system

The oxygen delivery system

- was started up approximately 6 weeks prior to BC-4 seeding
- was operated intermittently rather than continuously
- was effective at increasing DO (dissolved oxygen) levels above the < 1 mg/L initial condition

- had DO levels of generally more than 10 mg/L and in many cases more than 20 mg/L throughout the treatment zones; this was sustained over a year and is working well because the aquifer is sandy
- effectively increased oxygen levels in areas upgradient, downgradient, and cross-gradient to the target treatment zones
- affected some parts of the control plot

### Results of BC-4 biobarrier performance

Prior to BC-4 seeding of all test plots, MTBE concentrations remained relatively stable. After seeding and startup of O<sub>2</sub> injection:

- immediately downgradient of the seeded zone, MTBE concentrations decreased more than 90 percent
- other less dramatic declines in MTBE were observed upgradient of the seeded region where chemistry changes seasonally because of rainfall events
- no significant changes were observed in MTBE concentrations in the O<sub>2</sub> injection-only or control plots

Between 67 and 129 days after seeding (173 days following O<sub>2</sub> injection startup; see Figure 2), researchers observed:

- MTBE was not detected in many downgradient monitoring points
- several samples had MTBE concentrations ranging from 0.01 to 0.05 mg/L
- MTBE concentrations declined upgradient of the BC-4 and O<sub>2</sub> plot
- In the BC-4 seeded zone:
  - MTBE concentrations declined downgradient
- In the O<sub>2</sub> injection-only and control plots:
  - MTBE concentrations also declined
  - decreases also occurred where the O<sub>2</sub> delivery system caused an increase in DO concentrations
  - researchers hypothesized that the O<sub>2</sub> injection system stimulated the growth of naturally present MTBE degraders

### Conclusions

Researchers concluded that the time series data indicated EMB's effectiveness as a biobarrier to MTBE migration, and the barrier successfully intercepted the plume. "To our knowledge, this is the first successful field-scale demonstration of any engineered in-situ MTBE biodegradation process."

### Reference

Salanitro, J.P., Spinnler, G.E., Neville, C.C., Maner, P.M., Stearns, S.M., Johnson, P.C. and C. Bruce, "Demonstration of the Enhanced MTBE Bioremediation (EMB) In-Situ Process," paper presented at the 1999 Battelle Conference, April 19-22, San Diego, California; <http://www.battelle.org/environment/er/biosymp.html>.

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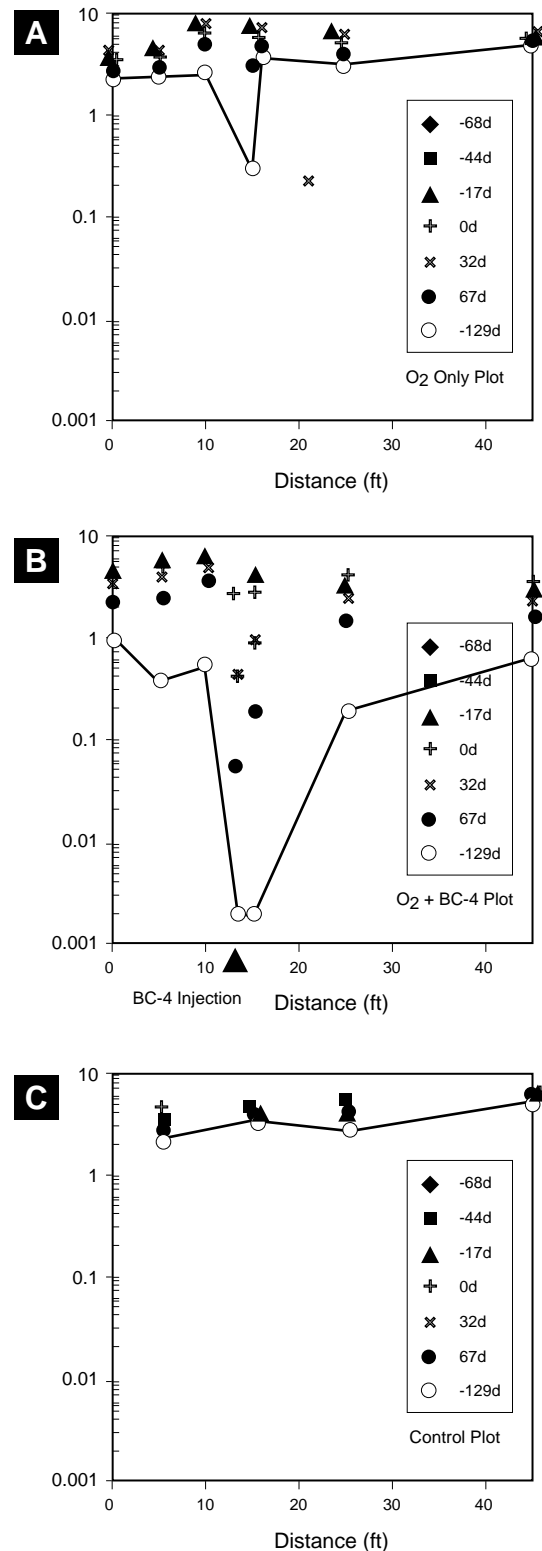


Figure 2. Mean MTBE concentration in shallow monitoring points: (a) O<sub>2</sub>-injection only plot, (b) O<sub>2</sub>-injection and BC-4 seeded plot and (c) the control plot (from Salanitro and others, 1999).



## MTBE biodegradation in biofilters

This article describes some of the first MTBE biofilter studies undertaken in the mid-1990s by Eweis and others (1997).

### Biofilter in Carson, California

A biofilter in Carson, California, which treated refinery wastewater discharge, developed the ability to degrade MTBE vapors. The biofilter, a publicly owned treatment work, received low concentrations of volatile organic compounds, including MTBE. The biofilter at Carson has the following characteristics:

- a height of 5 feet
- a diameter of 1 foot
- 3 feet of a compost-based media made up of 40 percent (by volume) compost (Kellogg's Nitrohumus®) and 60 percent (by volume) perlite
- inoculum provided by waste-activated sludge
- air supplied by a radial blower at a rate of 2.35 ft<sup>3</sup>/min, allowing for an empty bed residence time of approximately one minute

Workers collected samples from the biofilter using 10-liter Tedlar bags and analyzed the samples within six hours of sampling. After a year of operation, workers found the biofilter had developed the ability to degrade MTBE vapors, but little was known about the degrading microorganisms. Consequently, researchers engaged in a collaborative effort to

- investigate the feasibility of transferring and maintaining the activity of the degrading culture from the solid media in the biofilter into a liquid medium; a liquid culture would be necessary for the treating of contaminated groundwater
- determine the culture's nutritional and environmental requirements, particularly with regard to nitrogen

Researchers observed that nitrifying conditions increased MTBE removal efficiencies.

### Experimental study

Researchers obtained a 500 ml sample of compost from the Carson City biofilter and conducted solid and liquid phase studies. Cultures were grown in bottles, and MTBE spikes were added along with mineral salt solutions. The researchers monitored MTBE degradation for several weeks.

### Results

Researchers found the following:

- the MTBE-degrading culture from the biofilter degraded MTBE as a fixed film on a solid matrix and in the liquid culture
- biological treatment of MTBE in the liquid phase should be more economical than "air-stripping" with subsequent gas-phase control
- microorganisms grown in the medium containing nitrate as the nitrogen source appear to be more stable than those grown with ammonium as the nitrate source
- a pH decrease resulting from nitrification reactions that produce hydrogen ions may have adversely impacted the microorganisms; this is the probable reason for loss of MTBE biodegradability in the high ammonium medium
- degrading populations can be successfully grown in aqueous suspensions
- either ammonia or nitrate may be used as a nitrogen source
- future studies should identify
  - the specific microbial species involved
  - bacterial growth kinetics
  - kinetics of biodegradation

### Another pilot-scale biofilter study: MTBE-contaminated air

Eweis and others (1998) constructed a biofilter to treat MTBE-contaminated air. Following acclimation, the biofilter removed greater than 95 percent of the MTBE. Next they added toluene (a surrogate for BTEX) and observed the effect of the carbon source on MTBE removal.

### Process

Investigators inoculated the biofilter with an MTBE-degrading culture obtained from a compost-based biofilter. After 10 weeks, the biofilter removed 95 percent of the incoming MTBE-contaminated air. Inlet concentrations averaged 35 ppmv. MTBE was the sole carbon source for more than 180 days of operation, then toluene was introduced at a concentration of 8 ppmv. After 8 days, toluene concentration was increased to 25 ppmv, then to 70 ppmv for 8 days.

### Results

Two days after researchers added the toluene to the biofilter, 100 percent removal was achieved, although MTBE removal efficiency dropped somewhat, likely resulting from an increase in carbon mass loading rate and acclimation time.

When researchers again increased toluene to 70 ppmv, removal efficiency decreased to 70 percent; however, one hour after researchers cut off the toluene, MTBE removal efficiency increased again close to 100 percent. Eweis and others (1998) believe that "The immediate recovery of MTBE biodegradation indicated that it was not toxicity or substrate competition that had caused the drop in removal when toluene was present. It is believed that nitrogen limitation at the higher carbon load-ing rate was the cause. To investigate, researchers ran the biofilter for 4 weeks at 35 ppmv MTBE with no added toluene. Next MTBE concentration in the inlet was doubled. With the increase in the carbon mass loading rate, the same effect was observed, i.e. MTBE removal efficiency dropped gradually to less than 70 percent over the period of 8 days. A five-fold increase in the nitrogen concentration in the nutrient solution feed to the biofilter resulted in a recovery of biofilter performance. Why MTBE removal did not reach 100 percent is unclear; it could be due to channeling in the packing media in the biofilter or related to the elimination capacity of the column."

## Conclusions

Researchers concluded the following:

- bench-scale biofiltration successfully treated MTBE-contaminated air streams
- although toluene was degraded by the same organisms that degraded MTBE, it is unclear which organisms degraded each compound, and if the degradation proceeded along similar enzymatic pathways
- many questions remain, such as the feasibility of using microbial cultures for ex-situ or in-situ remediation

## References

Eweis, J.B., Chang, D.P.Y. and E.D. Schroeder, "Meeting the Challenge of MTBE Biodegradation," paper presented at the Air & Waste Management Association, 90th Annual Meeting & Exhibition, June 8-13, 1997, Toronto, Canada.

Eweis, J.B., Schroeder, E.D., Chang, D.P.Y. and K.M. Scow, "Biodegradation of MTBE in a Pilot-Scale Biofilter," paper presented at the First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 18-21, 1998, Monterey, California; 800-451-3543; press@battelle.org.



## Variability in BTEX plume biodegradation

Researchers recently studied a BTEX plume in intricate detail over a 5-year period. They had two objectives:

- to define the three-dimensional BTEX plume in this anaerobic aquifer
- to determine intrinsic remediation and biodegradation rates for individual organic compounds at various scales of the aquifer

The study (Davis and others, 1999) involved investigating year-to-year data variability of a plume in Western Australia. Results highlight the difficulty of defining plumes.

### Site characteristics

Groundwater at the site, in Perth, western Australia, was contaminated by a leaking UST that ceased operation in 1990. Hydrogeological characteristics of the site include:

- 7 to 12 m of medium to fine dune sand overlying a clay aquitard
- a layer of dark-brown iron-stained sands varying in thickness from 5 to 60 cm, found in the zone of water table fluctuation
- a water table that can fluctuate up to 1.8 m, increasing during winter rainfall
- annual rainfall of approximately 800 mm/yr
- a saturated aquifer thickness of 6 m
- local groundwater flow toward the southeast with a gradient of 0.003 to 0.0005
- groundwater velocity between 100 and 170 m/yr at the site vicinity
- hydraulic conductivity in the range of  $1.0 \times 10^{-4}$  to  $3.3 \times 10^{-4}$  m/s (8.6 to 29 m/day)
- effective porosity ranging between 0.26 and 0.3 m<sup>3</sup>/m<sup>3</sup>

### Investigation and monitoring

In the early 1990s, researchers installed 12 multiport monitoring (MP) boreholes, 11 within the perimeter of the plume and one upgradient. "Each MP borehole consisted of a bundle of 12 stainless steel tubes of internal diameter 2.5 mm slotted over the bottom 0.2 m." The slotted intervals on seven boreholes were spaced 0.5 m apart vertically; for five boreholes, the spacing was 0.25 m. Workers replaced boreholes obliterated when a UST was removed. They also installed an additional seven boreholes in 1995 to better define the plume width.

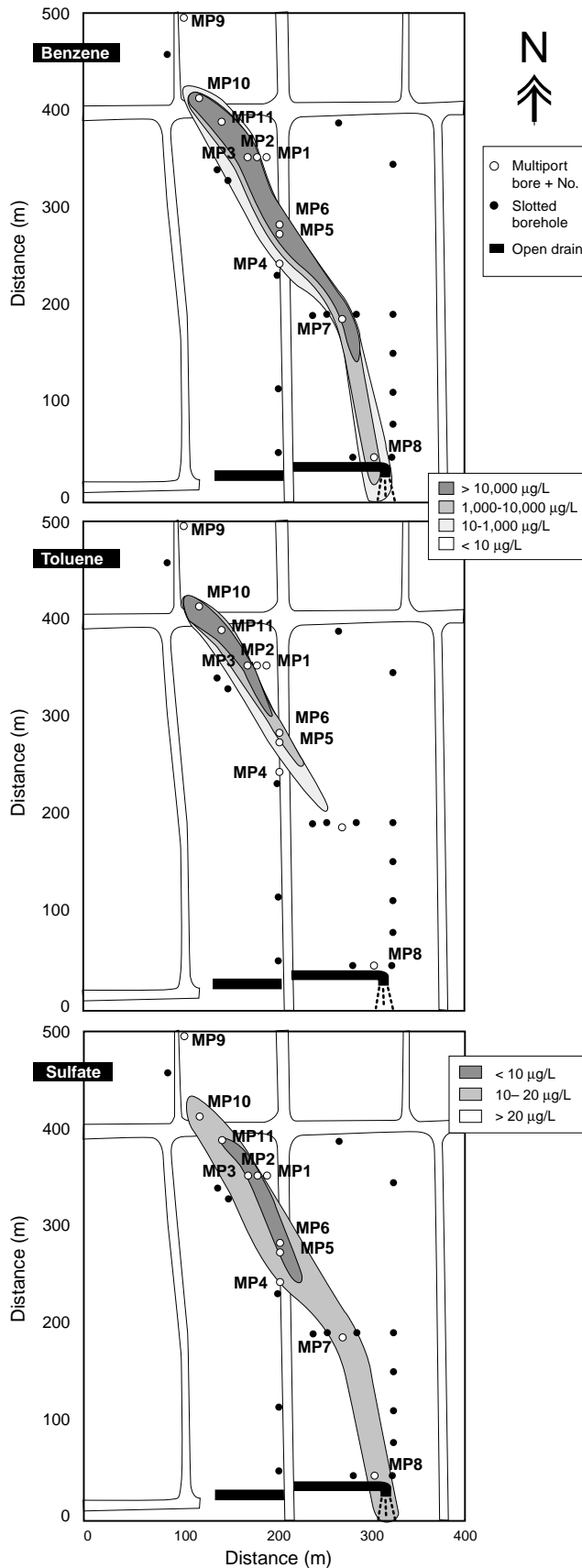


Figure 3. Benzene, toluene and sulfate plumes in April 1991. Also shows multiport bores (MP) and slotted boreholes (from Davis and others, 1999).

Field workers sampled groundwater from the boreholes every 1 to 2 months in 1991 and less frequently in subsequent years to determine seasonal trends. Researchers analyzed water samples for the following:

- BTEX compounds
- 1,3,5-trimethylbenzene (TMB)
- naphthalene
- degradation products such as methane, phenol, cresols
- inorganic compounds such as nitrate, sulfate, and iron

Field workers also recovered two intact cores about 30 m downgradient of the leaking tank " . . . to establish the vertical distribution and composition of any residual NAPL gasoline in the soil profile. The core was segmented into 5 to 10 cm sections, extracted with a diethyl ether and acetone mixture, and the extracts were analyzed by GC/MSD."

**Plume: physical characteristics and chemistry, organic and inorganic**

The plume was long and thin and varied vertically (Figures 3 and 4). In general, the April 1991 plume indicated

- benzene had a minimum length of 420 m, width of 20 to 50 m and thickness of 0.5 to 3 m
- toluene was less than 250 m in length and 0.5 to 2 m thick
- o-xylene's plume was similar to toluene's
- the m- and p-xylene plumes were similar to benzene's

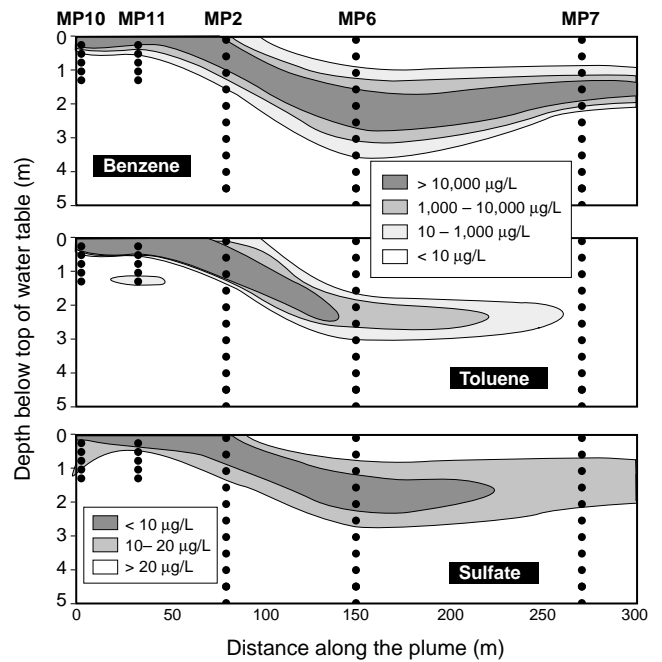


Figure 4. Cross-sections of benzene, toluene and sulfate plumes in April 1991 (from Davis and others, 1999) .

The plume had very steep concentration gradients, vertically and laterally, resulting either from small dispersion coefficients or microbial activity on the plume edges. "Longitudinal concentration gradients were shallower, although still significant in the highly contaminated portion of the plume between MP11 and MP12, about 50 m from the leak source. The longitudinal cross-sections also show a pronounced dip toward the base of the aquifer at about 80 m downgradient of the source." Here, up to 1 m of non-contaminated groundwater overlaid the plume, apparently due to enhanced rainfall recharge. This portion of the plume lies beneath a vacant lot whereas sealed surfaces exist elsewhere. "Even so, organic compounds were never detected at the base of the aquifer, which is only 6 m below the water table" (Davis and others, 1999).

Researchers also calculated ratios of the organic compounds to benzene, and found that with the exception of TMB (1,3,5-trimethylbenzene), other organics decreased along the plume length, but not uniformly. Analysis of core material taken from the water table zone indicated benzene concentration significantly depleted relative to other organic compounds. "... concentrations measured imply that residual NAPL was present in the recovered core, and therefore NAPL had moved downgradient from the point of leakage by up to approximately 30 m."

Davis and others (1999) also found "potential intermediate degradation products of m-, p- and o-xylene ... in the highly contaminated portion of plume, less than 80 m downgradient of the source between May 1991 and June 1992."

Inorganic analysis of the plume indicated the following:

- no systematic trends for  $\text{Fe}^{2+}$
- no methane detected in the plume
- mean dissolved  $\text{O}_2$  and  $\text{NO}_3^-$  concentrations were less than 0.6 mg/L and 0.2 mg/L respectively, inside or outside the plume; this may be a result of oxygen consumption and denitrification induced by high levels of organic carbon (OC) within the groundwater
- within vs. outside the plume, there was a significant decrease of Eh and sulfate and increased  $\text{HCO}_3^-$  and  $\text{H}_2\text{SO}_4^-$ ; depth profiles for a MP borehole 30 m downgradient of the source also show these trends

"Since mass loss of BTEX compounds was observed simultaneously with a drop in the Eh value, and there was production of  $\text{CO}_2$  and  $\text{H}_2\text{S}$ , as well as consumption of  $\text{SO}_4^{2-}$ , it is apparent that sulfate was acting as an electron acceptor for microbially enhanced degradation of the organic compounds ... Sulfate concentrations are substantially depleted at the center of the plume of organic compounds, in some cases to below 1 mg/L from background concentrations of 20 to 50 mg/L. Sulfate concentrations were always less than 15 mg/L and mostly less than 5 mg/L in regions of the plume with benzene concentrations greater than 100  $\mu\text{g/L}$ . Reduction of sulfate concentrations within the contaminated portions of the plume was also often accompanied by elevated  $\text{H}_2\text{S}$  concentrations up to 5.5 mg/L, compared with

below 0.1 mg/L outside the plume." This, along with the observed ratio of S to  $\text{SO}_4^{2-}$  "adds weight to the premise that S- $\text{SO}_4^{2-}$  is the predominant electron acceptor at the site, and indicates that other electron acceptors such as iron oxyhydroxides ( $\text{Fe}^{3+}$ ) on the aquifer matrix have either been significantly depleted within the plume or have played a minor role in the degradation process."

### Temporal changes

Researchers found that BTEX concentrations in boreholes were highly variable and "seemed to be strongly associated with seasonal movement of the water table." As the water table rose in the winter of 1992, shallower parts of one borehole showed increasing benzene concentrations. "The apparent plume thickness increased near the source over the period of groundwater rise. This was also observed for toluene and the other organic compounds ... these data seemed to reflect seasonal dissolution of organic compounds from entrapped NAPL within the near-water table zone, or highly contaminated capillary-zone water that was seasonally inundated by the water table. Based on data from MP10, Davis et al. (1993) also reported that the dissolved benzene mass increased in the near-water table soil profile over the 1992 winter period and over a full year. These data indicated that significant depletion of the BTEX and other organic compounds had not occurred near the source up to March 1992. Also, monitoring at a fine scale and in the capillary fringe was critical to assessment of loading rates to groundwater near what was a residual NAPL source in this zone" (Davis and others, 1999).

Although BTEX concentrations varied temporally in individual boreholes, ratios of TEX and naphthalene concentrations to benzene showed more consistent trends. "These ratios indicate that the large concentration changes observed over time at individual boreholes may have been due to hydraulic variations in water table heights and groundwater flow paths and perhaps also to variability in the contact zone of NAPL dissolution, or possibly variability of microbial degradation rates or sorption rates over time" (Davis and others, 1999).

Using simple, 1-dimensional modeling, researchers studied dissolution of benzene from the residual NAPL and identified three scenarios:

- using rate of removal as being proportional to the length of contact, and inversely proportional to the groundwater velocity, i.e., essentially the number of pore volumes that pass through the NAPL zone
- using velocity of the zone of mass transfer ( $V_{mtz}$ ) to predict benzene dissolution; this is the ratio of the dissolved compound  $i$  leaving the initial mass of compound within the NAPL, where
  - $V_{mtz} = qC_i / (d_i n S_i)$ , and
  - $q$  = Darcy velocity
  - $C_i$  = aqueous concentration of the  $i$ th component
  - $d_i$  = density of the  $i$ th component
  - $n$  = porosity
  - $S_i$  = saturation of the  $i$ th component

- using Mackay's method (outlined in the *Journal of Contaminant Hydrology*, Vol. 8, pages 23 to 42, based on partitioning/solubility) which estimates that dissolution of 90 to 99 percent of the NAPL benzene from the NAPL will occur within 100 to 400 years

These methods give benzene dissolution timeframes that are one to two orders of magnitude greater than that observed in the field; if non-equilibrium dissolution were observed, timeframes would be even greater. Researchers propose that the geometry of the NAPL, heterogeneity, source size and other loss mechanisms, such as volatilization at the time of the spill, could be critical in timeframe estimates.

**Significance of depth cross-sections**

Figure 5 shows depth cross-section concentrations of benzene, toluene and sulfate from April 1991 to March 1992 and to August 1994. The April 1991 and March 1992 concentrations are similar, likely because of season influences. Data from August 1994, however, which indicate significant benzene and toluene increases, show that "seasonal and

longer-term influences had altered groundwater flow directions and redirected the benzene plume around these borehole locations [MP1 and MP2] in March 1992. . . water table maxima and minima in the vicinity of the plume were quite dissimilar from year to year over the period of monitoring, especially the minima. Together, these observations indicate that year-to-year concentrations may be difficult to compare, and especially at individual boreholes, because of climatic variability between the years."

In addition, two small-scale tracer tests conducted near MP2 indicated a reorientation of the groundwater flow direction of approximately 20° between March-April 1991 (low water) and July-October 1991 (high water). "These trends are consistent with plume contouring and approximate seasonal groundwater flow direction changes. These transient features have significant implications for reliable monitoring of groundwater plumes, assessment of plume stability, and assessment of the effectiveness of intrinsic remediation in minimizing plume migration (*Davis and others, 1999*).

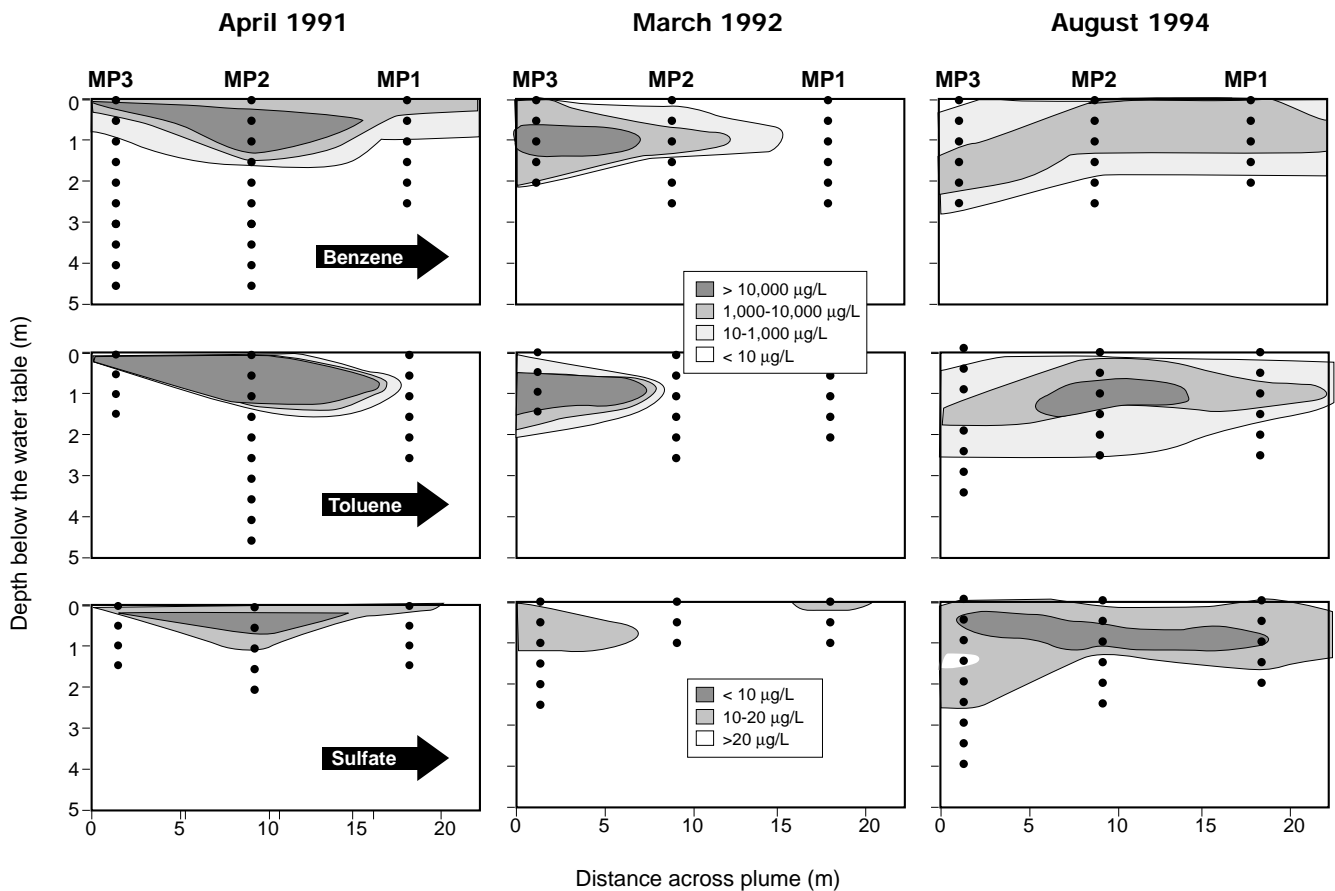


Figure 5. Cross-sections of the benzene, toluene and sulfate plumes in April 1991, March 1992 and August 1994. Dots indicate monitoring port locations (from Davis and others, 1999).

## Estimates of degradation rates

Degradation in this plume is indicated by the following:

- systematic decreases of  $S-SO_4^{2-}$  concentrations
- increases in  $HCO_3^-$  concentrations
- presence of degradation products in plume sections where BTEX concentrations are high
- extent of the benzene plume compared to plumes of some other organic compounds (although preferential dissolution or sorption may have a role)

Table 2 shows degradation rates derived from using a tracer test using deuterium-labeled benzene, toluene, p-xylene and naphthalene, 3-dimensional analytical modeling, and estimates compiled by Howard and others (*Handbook of Environmental Degradation Rates*, Lewis Publishers).

Compound	Tracer test estimates	Model estimates	Howard and others compilation <sup>1</sup>
Benzene	> 800	> 800	112–720
Toluene	100 ±40	122 ±25	56–210
Ethylbenzene	–	230 ±30	176–228
p-xylene	225 ±75	–	–
m- and p-xylene	–	170 ±10	28–112
o-xylene	–	125 ±10	180–360
1,3,5-trimethylbenzene	–	180	–
Naphthalene	33 ±6	160 ±20	25–258

<sup>1</sup> Reviewer's note: Howard and others data may not be as reliable as the other data in this table.

**Table 2. Degradation rates for various hydrocarbon compounds (from Davis and others, 1999).**

Researchers also approximated degradation rates or half-lives on a larger scale than the tracer test. Estimates shown in Table 3 were made with the following assumptions:

- steady state conditions
- small lateral dispersion
- insignificant sorption
- average groundwater velocity or specific discharge at the site assumed to be about 150 m/yr

Researchers found that half-life estimates varied in different zones of the plume. For instance, toluene had a half-life range (110 to 260 days) while the range for o-xylene was 160 to 400 days. Toluene's shortest half-life was 80 to 150 m downgradient of the source, while m- and p-xylene indicated shortest half-lives at 30 to 80 m downgradient.

Compound	MP borehole interval (m) (interval distance-m)			
	30-80 (50)	80-150 (70)	150-260 (110)	260-420 (160)
Toluene	140	110	260	200
Ethylbenzene	780	> 800	550	650
m- and p-xylene	130	–	340	490
o-xylene	160	400	280	220
1,3,5-trimethylbenzene	420	–	> 800	270
Naphthalene	280	730	730	26

**Table 3. Degradation rates determined on a larger scale (from Davis and others, 1999).**

Each method for estimating half-life had limitations:

- The tracer test gave a small-scale estimate but provided reliable in-situ measurements.
- The plume-scale modeling assumed uniform velocities and aquifer properties and required approximation of average dissolution rates for the organic compounds and source dimensions.
- The between-borehole estimates relied on a uniform velocity and assumed benzene was reasonably conservative.

Researchers found, however, that comparison between the methods was good.

## Conclusions

Researchers concluded the following:

- Fine-scale monitoring using multiport boreholes enabled scientists to define long, thin hydrocarbon plumes in sulfate-rich anaerobic groundwater.
- The plume defined had extremely high concentration gradients.
- Thin plumes would be difficult to monitor with long-screened (1 m screened) piezometers.
- Such high concentration gradients were apparently maintained by very low dispersion coefficients in this uniform sand aquifer; they might also be sustained by enhanced degradation of hydrocarbon compounds along the plume periphery.
- Contoured concentration data for the 5-year period indicated that toluene and o-xylene plumes were at best only partially steady-state due to seasonal groundwater flow changes.
- Temporal variations appeared to occur from hydraulic variations and seasonal water table rises, but also from preferential dissolution and biodegradation.

- Data showed a periodic influx of dissolved hydrocarbons to groundwater near the source due to water table rise and to inundation of NAPL resident within the near-capillary zone of the aquifer.
- Periodic or sporadic changes in groundwater flow direction also significantly changed BTEX concentrations at individual borehole locations; these transient features have significant implications for reliably assessing the effectiveness of intrinsic attenuation/biodegradation in minimizing plume migration and establishing plume stability.
- Toluene showed significant biodegradation.
- Conclusive evidence of benzene biodegradation did not exist.
- Ratios of hydrocarbon/benzene concentrations were more reliable than ratios of other compounds in estimating between-borehole scale degradation rates; without a relatively conservative tracer or groundwater movement, such as benzene, the intrinsic bioremediation rate estimates based on between-borehole concentration reductions could lead to significant degradation rate errors

Where groundwater flow directions vary seasonally the probability that boreholes along a plume will intersect the same flow-path is small, unless boreholes are very closely spaced, or if significant pumping occurs during sampling to capture passive flow-paths

Preferential intrinsic biodegradation of selected organic compounds within the BTEX plume occurred in parallel with sulfate reduction and bicarbonate production

The ratio of hydrocarbon concentrations to benzene also indicated that the residual NAPL composition was changing over time

The depletion of residual NAPL had a potential significant role in influencing relative plume dimensions and groundwater composition, and therefore, in assessment of intrinsic remediation these data emphasize the need to define and target the residual NAPL in any remediation because of its longevity

- Strong evidence suggested preferential natural biodegradation of TEX and other organic compounds within the plume, with sulfate acting as the principal electron acceptor.
- Toluene and o-xylene plumes were pseudo-steady state and substantially intrinsically bioremediated; still the plume migrated significantly off-site.
- Modeling suggested that the benzene plume would not be at steady state until it had extended to a distance beyond 4 km.

In addition, researchers state that " At this site, high concentrations of the dissolved hydrocarbons may therefore persist (especially for benzene ) in groundwater for large distances downgradient of the source. . . The data have significant implications for sites where it may be wrongly concluded, from limited and spatial and temporal monitoring, that intrinsic remediation is occurring. The long-term trend in the organic compound concentrations also provides indications of the longevity of residual NAPL in the near-water table zone as a source for dissolved BTEX compounds in groundwater."

" Temporal data from frequent monitoring of groundwater chemistry at carefully placed boreholes combined with spatial mapping (and perhaps modeling) of plumes seems essential to adequately assess the extent of intrinsic remediation . . . Data from a small number of short-screened piezometers or single boreholes, whether close to the source of leakage or further downgradient, were unreliable as the sole evidence for assessment of intrinsic remediation of constituent organic compounds. This was because of the significant plume variability in time and space, and possibly because of artifacts introduced through pumping and sampling."

## Reference

Davis, B., Barber, C., Poer, T.R., Thierrin, J., Patterson, B.M., Rayner, J.L. and Q. Wu, " The variability and intrinsic remediation of a BTEX plume in anaerobic sulfate-rich groundwater," *Journal of Contaminant Hydrology*, Vol. 36, 1999, Elsevier Science; P.O. Box 7247-7682, Philadelphia, Pennsylvania 19170-7682; <http://www.elsevier>.



## EPA's monitored natural attenuation directive 9200.4-17P

In April 1999, the EPA Office of Solid Waste and Emergency Response issued its final directive (9200.4-17P) on the use of monitored natural attenuation (MNA). This directive supercedes the interim draft directive issued in December 1997. The final directive's notice of availability, recently published in the *Federal Register*, is on the Web at <http://www.epa.gov/swrust1/directiv/d9200417.htm>. *UTTU* published a summary of the interim directive in its March/April 1998 issue.

Salient differences between the final and interim directives follow. The final directive

- does not address remediation of contaminated sediments; however, it states that many of the principles regarding contaminated water would apply to contaminated sediments
- provides guidance on defining contaminant plumes:
  - plumes are defined for each contaminant of concern "based on chemical concentrations above which the overseeing regulatory authority has determined represent an actual or potential threat to human health or the environment" (see footnote 2)
  - uncertainty in measuring plume boundaries should be considered in determining plume
  - plume stability; "for example, a plume is typically delineated for each contaminant of concern as a 2- or 3-dimensional feature; plumes are commonly drawn by computer contouring programs, which estimate concentrations between actual data points; EPA recognized that a plume boundary is more realistically defined by a zone rather than a line; fluctuations within this zone are likely to occur due to a number of factors (e.g., analytical, seasonal, spatial, etc.) that may or may not be indicative of a trend in plume migration; therefore, site characterization activities and performance monitoring should focus on collection of data of sufficient quality to enable decisions to be made with a high level of confidence" (see footnote 19)
- strengthens language on remediation objectives—the objective is preventing contamination migration rather than minimizing migration (see footnote 5)
- explicitly defines source material as "material that includes or contains hazardous substances, pollutants or contaminants that act as a reservoir (either stationary or mobile) for migration of contamination to the groundwater, to surface water, and/or to air (or other environmental media) or that act as a source for direct exposure; contaminated groundwater generally is not considered to be a source material although non-aqueous phase liquids (NAPLs occurring either as residual- or free-phase) may be viewed as source materials" (see footnote 6)
- adds radioactive decay to list of in-situ natural attenuation processes
- states that appropriate selection of MNA requires evaluation of all contaminants that represent an actual or potential threat to human health or the environment
- adds a section on "cross-media transfer" noting that
  - destruction of contaminants is preferred over transfer to another media
  - where contaminants are transferred, workers should conduct a risk-assessment and long-term monitoring of the affected media
  - remedial action decisions should include opportunities for public involvement to both educate and gather feedback from interested parties
- stresses requirement for data of known quality:
  - the level of confidence on calculated attenuation rates should be documented
  - statistical confidence intervals should be estimated for attenuation rates
  - sensitivity analyses should be performed to determine dependence of calculated remediation timeframes on uncertainties in rate constants and other factors
  - for environmental decision-making, data must be of adequate quality and usability for their intended purpose
- provides guidance to determine a reasonable timeframe for achieving remediation objectives; it should be comparable to that which could be achieved through active remediation
- states that the most appropriate timeframe must be determined by analysis of all appropriate remedy alternatives
- offers guidance for restoration of groundwater to beneficial uses: a comparison of restoration alternatives from most aggressive to passive is necessary to establish time span required to achieve remediation objectives
- stresses that a measured decrease in contaminant concentrations of at least one order of magnitude is necessary to determine appropriate rate law, to describe rate of attenuation, and to demonstrate that the estimated rate is statistically different from zero at a 95 percent level of confidence
- recognizes that longer timeframes often associated with MNA remedies produce higher levels of uncertainty; thus, adequate performance monitoring and contingency remedies are important
- states that performance monitoring should continue until remediation objectives have been achieved, and longer if necessary, to verify that the site no longer poses a threat to human health or the environment



## Research notes

This new section of UTTU summarizes articles describing relevant research published in peer-reviewed journals.

**Anaerobic biodegradation of long-chain n-alkanes under sulfate-reducing conditions**, Caldwell, M.E., Garrett, R.M., Prince, R.C. and J.M. Suflita, *Environmental Science and Technology*, Vol. 32, No. 14, 1998; 703-552-0685; <http://www.pubs.acs.org>.

Researchers in this laboratory study explored "the limits of anaerobic hydrocarbon metabolism and helped lay the foundation for future biomarker studies. They monitored the anaerobic biodegradation of C<sub>15</sub> to C<sub>34</sub> n-alkanes (from a weathered crude oil) under sulfate-reducing conditions using gas chromatographic analysis to confirm that the n-alkanes had been removed. The mineralization of the n-alkane fraction of the hydrocarbon was confirmed using <sup>14</sup>C-14-15-octacosane (C<sub>28</sub>H<sub>58</sub>) with 98 percent of the radioactivity recovered as <sup>14</sup>CO<sub>2</sub>."

Researchers used as an inoculum a marine sediment known to harbor a metabolically diverse microflora capable of hydrocarbon metabolism. As a carbon source they used a highly characterized weathered crude oil. This mixture resembled those which "typically get deposited on beaches and in sediments following the abiotic removal of the more volatile and water-soluble components." Thus, the oil was essentially devoid of lower molecular weight hydrocarbons. Researchers also noted that "the extent of this metabolism is comparable to what has previously only been observed in studies of aerobic hydrocarbon decay."

**Field demonstration of permeable wall flushing for biostimulation of a shallow sandy aquifer**, Devlin, J.F. and J.F. Barker, *Ground Water Monitoring and Remediation*, Winter, 1999; 800-332-2104; <http://www.ngwa.org>.

Workers installed a pilot-scale (4 by 4 by 1 meters) nutrient injection wall (NIW) in the Borden Aquifer (see UTTU Vol. 13, No. 4, for a description of the BTEX/MTBE aquifer). Such walls can be installed across the entire width and depth of a contaminant plume (here it was not) and be instrumented with injection and withdrawal wells. At the Borden site, researchers injected potassium acetate into the wall to stimulate anaerobic microbes. After approximately 6 hours of injection and withdrawal (representing one pore volume) the wall was flushed with "reasonable uniformity." "Calculations based on head level data collected during the flushing and on

the solute breakthrough curves" indicated that about 90 percent of the flow induced by the pumping and injecting was confined to the permeable wall. These results show that a permeable wall injection system is a viable method of introducing solutes uniformly to a cross-section of an aquifer, with minimal perturbation of the natural flow system."

"During the passive intervals (which can be up to 99 percent of the time) the slug of remedial solution is transported out of the wall and carried by the natural flow of groundwater. As the slug is transported, it undergoes longitudinal dispersive mixing with the natural groundwater and any pollutants present. The spreading of sequentially injected slugs leads to the creation of a zone in the aquifer, downgradient and outside the wall, in which microorganisms receive a continuous supply of required nutrients. This method of injection minimizes the displacement of contaminated water so that dispersive mixing can occur over minimal distances downgradient from the wall. Since stable pulses mix, the bioactive zone in an aquifer is established at some distance away from the injection wells and the NIW." This procedure also minimizes biofouling at the wells because the bioactive zone is some distance from the injection wells.

**Utilization of biomass residues for the remediation of metal-polluted soils**, Fischer, K., Bipp, H.P., Riemschneider, P., Leidmann, P., Bieniek, D. and A. Kettrup, *Environmental Science and Technology*, Vol. 32, No. 14, 1998; 703-552-0685; <http://www.pubs.acs.org>.

Researchers in Germany experimented with biomass residues as a source for natural chelates to improve leaching techniques for remediation of metal-polluted soils. Researchers had two objectives:

- to examine the capability of residue formulations to extract Cd, Cr, Cu, Ni, Pb and Zn from polluted soils under various physicochemical conditions
- to determine the bonding-type specific depletion of the metals from soils

Residues studied included molasses, blood meal and silage effluents. Researchers found that grass silage effluent removed about 75 percent of the Cd and greater than 50 percent of the Cu and Zn from contaminated soils. The neutral blood meal hydrolysate extracted primarily Cu (55 to 66 percent) and Ni (38-67 percent). Laboratory workers used a sequential leaching procedure to identify metal bonds attacked. Hydrolysates containing sugar acids mobilized Cu and Pb under alkaline conditions. "The actual results support the conclusion that biomass residues have a potential to serve as extractants in remediation techniques."



## State symposium on MTBE and fuel oxygenates

The ASTSWMO MTBE Workgroup sponsored a 2-day MTBE symposium in Washington D.C., July 26-27, 1999. The use of RFG (federal reformulated gasoline, usually containing MTBE) was mandated in the 1990 Clean Air Act Amendments in certain areas of the country experiencing air contaminant problems. RFG helps gasoline burn cleaner and reduces carbon monoxide and other atmosphere-deteriorating compound emissions. Conclusions and recommendations from the symposium are outlined in the following sections:

- MTBE occurrence
- MTBE characterization
- MTBE remediation
- MTBE health facts/studies
- MTBE proposed substitutes (ethanol and TAME, DIPE and ETBE)
- summary of EPA's Blue Ribbon Panel on fuel oxygenates
- discussion groups

**MTBE occurrence.** The following conclusions and recommendations were reached:

- low concentrations of MTBE are frequently found in ambient groundwater (groundwater sampling by the USGS in the National Water Quality Assessment program) and community water supply wells in some high MTBE-use areas; of the 2,743 wells tested, 2,598 wells had concentrations with a 21 percent detection in high use areas (0.2 µg/L or greater) and a 2.3 percent detection in low/no use areas
- some MTBE-contaminated community water supplies and domestic wells have had to be removed from use, or treatment has been necessary
- a variety of sources are responsible for the occurrence of MTBE in groundwater
- in the United States, about 3.5 percent by volume of every gallon of gasoline is MTBE
- MTBE is the most commonly used oxygenate; ethanol is second; ETBE, TAME, DIPE and TBA are used to a lesser extent
- the source of MTBE is often difficult to define and not limited to a point-source such as a LUST; MTBE has been found in stormwater, streams, lakes (gas from motorboats), the atmosphere, and even as the result of small spills such as car accidents; sources include refineries, pipelines, storage tanks, accidental spillage, homeowner disposal, emissions during fueling, vehicle emissions, vehicle evaporative losses, atmospheric deposition, urban runoff and recreational watercraft

- vehicle emissions to the atmosphere are about 40 kg MTBE/yr
- the hierarchy of MTBE groundwater contamination is:
  - point source release, > 100,000 µg/L
  - recreational watercraft, 10-15 µg/L
  - non-point sources such as atmospheric deposition and urban runoff, 1-10 µg/L
- states have been finding MTBE in areas where MTBE was not expected
- distributors' verification of gasoline composition is often difficult to obtain because supplies travel in pipelines, supplies are traded and formulas are proprietary
- MTBE contamination is a problem in some states and not in others; part of this may result from inadequate MTBE sampling

**MTBE characterization.** The following conclusions/recommendations were reached:

- some states have no regulations requiring MTBE monitoring, and many are waiting for a standard from OUST; a standard will not likely be available until completion of health/environmental testing, which could take up to 5 years (the OUST health advisory standard of 20 to 40 µg/L is not enforceable—it is merely an advisory)
- some states have developed their own standards, using a taste and odor threshold that varies from about 5 µg/L to 70 µg/L; drinking water regulations and guidelines as a whole vary from about 5 to 240 ppb; the EPA has published a map indicating drinking water regulations and guidelines for each state, and some states have no guidelines/regulations (see Figure 6)
- most states have MTBE cleanup levels, determined by their state LUST program
- EPA is collecting and organizing data, and facilitating state coordination between drinking water and UST programs
- some states, including California, are not required to monitor for surface water
- in California, however, MTBE groundwater detections greater than 2 to 3 ppb warrant shutting down a well because the low concentrations indicate a plume
- in areas of high recharge, diving MTBE plumes might be expected, and sometimes only a careful site investigation/characterization will find the plume

**MTBE remediation.** The following conclusions/recommendations were reached concerning remediation:

- active remediation of MTBE may be required at some gasoline release sites where MTBE has migrated much farther than conventional gasoline hydrocarbons
- sites contaminated with MTBE typically increase the cost of a typical gasoline remediation by tens of thousands of dollars



- techniques that work for BTEX remediation do not necessarily work for MTBE remediation because of MTBE's high solubility and resistance to biodegradation
- MTBE can persist for up to 20 years, if not longer
- air sparging has a 50 percent success rate; pump-and-treat has a greater success but is more costly
- one researcher showed that cored live oaks above an MTBE groundwater plume contained MTBE; the trees, which take up to about 100 gal/day of water, acted as a natural pump-and-treat and SVE system, indicating that phytoremediation could be a viable remediation strategy as long as groundwater flow is slow enough, about 1 to 10 ft/yr
- half-life of MTBE in air is on the order of a few days because of photo-oxidation
- MTBE can be biodegradable under certain conditions; however, the appearance of BTEX will slow MTBE biodegradation
- ground/surface water (i.e., stream or lake) interfaces can cause rapid microbial degradation of MTBE

**MTBE health facts/studies.** Conclusions/recommendations include the following:

- health studies have been inconclusive; therefore it is difficult to characterize MTBE's health risks
- California's MTBE health study involving about 125 people was basically a literature search; the study specifically addressed California's problems
- MTBE studies have involved only small populations
- testing needs to consider the population exposure distribution and "high-end" exposure scenarios
- many negative effects of MTBE exposure have been found to be short-lived
- although MTBE has been found to produce tumors in rats (and other chronic and acute effects), to extrapolate the data to humans may not be valid because rats contain a unique protein not present in humans; thus, relevance of the rat study's applicability to humans is debatable
- exposure thresholds in humans appear to be 24 to 135  $\mu\text{g/L}$  for taste and 15 to 180  $\mu\text{g/L}$  for odor
- there is no data on ingested oxygenates in humans (except for ethanol)
- the MTBE inhaled reference concentration without systemic effect is 3  $\text{mg/m}^3$ ; daily chronic exposure is thought to be a few micrograms/ $\text{m}^3$
- information to support MTBE's listing as a carcinogen is insufficient

- EPA's MTBE standard is a drinking water advisory of 20 to 40  $\mu\text{g/L}$
- to further assess health effects of MTBE/other oxygenates, researchers should consider the following:
  - extrapolating data to oral data
  - performing sub-chronic/chronic studies of MTBE
  - assessing ethanol impact; no formal studies have been conducted, but exposure is not expected to be high enough to contribute to health problems
  - assessing the impact of TBA
  - assessing susceptible sub-populations

**MTBE proposed substitutes (ethanol and TAME, DIPE and ETBE).** Conclusions/recommendations include:

#### *Ethanol*

- must be blended at the stations but has stability problems in hot weather
- is infinitely soluble in water and does not sorb to aquifer material
- is readily biodegraded, except at high concentration (> 10 percent)
- may increase cost of gasoline by 6 or 7 cents/gal
- supplies in the United States are not sufficient to replace all MTBE use, and the infrastructure does not exist to supply ethanol

#### *TAME, DIPE and ETBE*

- health effects are unknown
- solubilities in water are lower than MTBE but still high
- sorption to aquifer material and transport velocities in water will be similar to benzene
- rapid degradation is not expected
- compounds have the potential for long-range transport

#### **Summary of EPA's Blue Ribbon Panel on fuel**

**oxygenates.** Patricia Ellis (Delaware Department of Natural Resources and Environmental Control) and John Zogorski (U.S. Geological Survey) summarized EPA's Blue Ribbon Panel findings. The Blue Ribbon Panel was formed in November 1998 to investigate air and water quality concerns associated with oxygenated gasoline, and to provide recommendations on how to achieve the air/water quality protection goals. The panel, which met six times, concluded the following:

- the distribution, use and combustion of gasoline poses risks to the environment and public health
- RFG provides considerable air quality improvements and benefits for many U.S. citizens

- the use of MTBE has raised the issue of health/environmental effects of both MTBE alone and MTBE in gasoline; MTBE's persistence and mobility in water pose disproportionate risks of contaminating ground and surface water when compared to other gasoline components
- MTBE has been found in a number of water supplies nationwide, primarily causing odor and taste concerns that have led water suppliers to reduce use of those supplies; in addition, incidents of MTBE in drinking water supplies at levels causing immediate public health concerns have occurred, but these are rare; the panel believes that the occurrence of MTBE in drinking water supplies can and should be substantially reduced
- MTBE is an integral component of the U.S. gasoline supply both in terms of volume and octane; changes in its use, with the attendant capital construction and infrastructure modifications, must be implemented with sufficient time, certainty, and flexibility to maintain the stability of both the complex U.S. fuel supply system and gasoline prices

The panel prepared the following recommendations:

- enhancing water protection, including prevention, treatment and remediation
- blending fuel for clean air and water and including the oxygen requirement
- maintaining air benefits
- reducing the use of MTBE and reducing the use of the wintertime Oxyfuel program
- evaluating and learning from experience

The panel's findings and recommendations, finalized in July 1999, consist of summary papers on the following topics:

- water contamination
- air quality benefits
- fuel supply and cost
- comparison of the fuel additives
- prevention, treatment and remediation

The documents are on the Blue Ribbon Panel web page, <http://www.epa.gov/oms/consumer/fuelsoxypanel/blueribb.htm>.

**Discussion groups**

Near the meeting's end, Jeff Kuhn, a symposium organizer, divided participants into four groups and asked each group to identify four most critical MTBE concerns. These included:

1. Determining a national standard for MTBE, giving states the authority to test ground and surface water for MTBE and to delimit cleanup levels
  - this includes doing toxicology/cancer studies for MTBE and MTBE degradation products
2. Expanding testing of MTBE to public water supplies with the goal of creating an MTBE national database to understand the magnitude of the problem

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3. Determining MTBE's impacts on present funding, and finding future sources for MTBE characterization and remediation studies
  - funding should exist for remediation, alternative drinking water supplies, state staffing and UST inspections
  - funding should be found for additional studies
  - EPA should release funding to states
4. Identifying and validating MTBE remedial technologies that are most effective and cost-effective, and compilation of this data into a meaningful document
5. Gathering information on how to complete a better site characterization given MTBE's behavior in the surface and subsurface
6. Bringing regulated USTs and other MTBE containments into compliance and evaluating the effectiveness of the 1998 upgrades
7. Determining an appropriate MTBE substitute for which health effects are known or could be known before implementation
8. Need for refiners/distributors to disclose formulas to aid in identification of components in petroleum products
9. Education and information exchange in terms of:
  - educating communities with respect to MTBE issues, such as pollution prevention, MTBE characterization and remediation and wellhead protection
  - establishing communication between the various state agencies
  - holding more symposiums like this one to share data and experiences

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