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General information on MTBE

In March 1999, Governor Davis of California announced his intentions to phase out the use of MTBE in gasoline by late 2002. Based on California's scientific studies of the environmental effects of MTBE, the governor concluded that "the additive is a danger to the environment and will increase the pressure on the federal government to lift its oxygenate requirement." The governor's actions may affect other state environmental programs with respect to the creation of new state drinking water and groundwater cleanup standards for MTBE (*Lucas, 1999*).

As of 1994, 30 percent of the gasoline used in the United States contained added oxygenates. By virtue of its low cost, ease of production and favorable transfer and blending characteristics, MTBE has become the most commonly used fuel oxygenate (*U.S. EPA Fact Sheets, 1997 and 1998*).

What is MTBE?

Methyl tertiary-butyl ether (MTBE or MtBE) is a volatile organic chemical made by combining methanol and isobutylene. The methanol is typically derived from natural gas while the isobutylene is a byproduct of the petroleum refinery process. Since 1979, MTBE has been used as an octane enhancer in gasoline. MTBE was initially used as a replacement for lead, primarily in mid- and high-grade gasoline at concentrations as high as 8 percent by volume. At higher concentrations, 11 to 15 percent by volume, it is used as a fuel oxygenate (*Squillance and others, 1998*).

MTBE occurrence

The major point sources of MTBE contamination are from LUSTs. Potential nonpoint sources of MTBE include precipitation, urban runoff and water craft. Once MTBE is in the water, it moves between surface and groundwater with the natural movement of water. MTBE concentrations as high as 200,000 µg/L have been measured at a LUST site; previously, however, routine groundwater monitoring at UST sites has focused on the BTEX compounds (*Zogorski and others, 1996*).

Most MTBE detections occur in shallow groundwater and in urban areas. Recently, however, substantial contamination has been found at depth, such as in the Santa Monica well field. Ninety-nine percent of wells sampled from shallow groundwater in agricultural areas did not have MTBE.

As for air occurrence, "MTBE and other fuel oxygenates are not included in routine ambient air monitoring done by local and state agencies. An exception is the state of California, which just recently began to monitor for MTBE and other volatile organic compounds (VOCs) in ambient air. Air-quality data have been collected for MTBE in six cities as part of special studies. These data are not sufficient to provide a

national perspective; however, MTBE was found in urban air and the median concentrations within these urban areas ranged between 0.13 and 4.6 ppb by volume. Concentrations of MTBE in the air near known sources of MTBE (gasoline stations, roadways, parking lots and garages and so forth) are higher, and in many cases, considerably higher than ambient urban air" (*Zogorski and others, 1996*).

"Because of their occurrence in the atmosphere, and favorable and rapid partitioning to water, fuel oxygenates will occur in precipitation in direct proportion to their concentrations in air. Changes in the ambient air concentration of MTBE, due to increased or decreased usage of oxygenated gasoline, for example, will affect the level of MTBE in precipitation." As temperatures cool, MTBE concentration in precipitation increases. "Assuming a concentration of 1 ppb by volume MTBE in the atmosphere, the concentration of MTBE in precipitation would increase almost tenfold, from about 0.2 to 1.5 µg/L, if the temperature decreased from 20° to 0° degrees Celsius. Based on this range of proportionality and MTBE atmospheric concentration data collected in a few cities, precipitation for general urban atmospheres could contain sub-µg/L to about 3 µg/L MTBE. Theory predicts that precipitation concentrations will be higher near stations that consistently experience higher air concentrations of MTBE. Data suggest that the alkyl ether oxygenates have lifetimes in the atmosphere that range from 4 days to 2 weeks. The main degradation pathway seems to be reaction with hydroxyl radical to form tert-butyl formate. In summary, the atmospheric source of alkyl ether oxygenates in urban areas is believed to be continual, and results in low concentration of MTBE in water relative to point sources such as USTs. The atmospheric source is also areally extensive due to the dispersive effect of weather patterns."

"Precipitation inputs oxygenates directly to streams, rivers, lakes and reservoirs as it falls on these surface water bodies or enters surface water through overland runoff and stormwater drainage. Little data exist on the occurrence of any of the fuel oxygenates in surface-water bodies. Scientists do know, however, that when MTBE volatilizes from water, MTBE in large rivers and some streams will not be lost quickly by volatilization. Precipitation falling on land and recharging aquifers, together with diffusion of oxygenates from the atmosphere through the unsaturated zone, inputs oxygenates to shallow groundwater. From shallow groundwater, it is possible that dissolved alkyl ether oxygenates **will move deeper into an aquifer system toward wells** and surface water discharge areas. The concentration of an oxygenate in groundwater along a particular flow path depends upon the age of groundwater, that is its residence time in the aquifer from recharge location and rate of biodegradation reactions. Dissolved MTBE and other alkyl ether oxygenates will advance deeper into the aquifer system than BTEX compounds because they are less degradable than BTEX compounds; however, the significance of this deeper migration is uncertain because of the paucity of in-situ monitoring and degradation studies" (*Zogorski and others, 1996*; see also the article "MTBE/BTEX plume evolution as defined by three sampling events.")

The U.S. Geological Survey also measured MTBE in storm waters in cities with populations greater than 100,000. Northeastern cities and California were not included in this study. MTBE was detected in about 7 percent of the 592 stormwater samples. When detected, concentrations ranged from 0.2 to 8.7 µg/L with a median of 1.5 µg/L. Eighty-three percent of the detectable concentrations occurred during the winter season (*Zogorski and others, 1996*).

“The maximum concentration of MTBE detected in storm-water is about five orders of magnitude below the median lethal concentration for the most sensitive species investigated to date. More toxicity studies of aquatic animals and plants, bioaccumulation information and ambient levels in surface water are needed before the significance of MTBE to aquatic life can be assessed” (*Zogorski and others, 1996*).

In another study (*Reiser and O'Brien, 1998*), field workers took 112 samples from several streams that drained a variety of land use settings in New Jersey. They detected a total of 47 VOCs. The most frequently detected VOC was MTBE in 78 percent of the samples. They found MTBE concentrations higher in the cooler months, which they attributed to MTBE's lower volatility and greater partitioning of MTBE from air to water at cooler temperatures. In addition, MTBE is generally used in greater volumes in gasoline during the winter months in New Jersey. Workers found that MTBE concentrations were not significantly correlated with flow at any of the sites. MTBE concentrations did not appear to be related to percentage of urban-industrial land use. “Although all VOC concentrations measured met existing water-quality criteria . . . criteria for aquatic life have been established for only 26 or the 47 compounds detected. In addition U.S. EPA criteria apply only to individual compounds, but most samples contained more than one VOC. **The long-term cumulative and synergistic effects of low concentrations of multiple compounds on human and aquatic health is an area of active research**” (*Reiser and O'Brien, 1998*).

Physical and chemical characteristics

Following are lists of MTBE's physical and chemical characteristics, including solubility and adsorbivity, transport features, volatility and biodegradability (*U.S. EPA Fact Sheets, 1997–98*).

Solubility and adsorbivity of MTBE

- MTBE is about 30 times more soluble than benzene in water; its effective solubility is higher when gasoline is present
- pure MTBE can reach an equilibrium concentration in water of approximately 5 percent, i.e., 48,000 mg/L
- at 25°C, the water solubility of MTBE is about 5,000 mg/L for a gasoline that is 10 percent MTBE by weight
- MTBE is much less likely than benzene to adsorb to soil or organic carbon (Log K_{ow} MTBE is 1.20; log K_{ow} benzene is 2.13)
- MTBE's relatively high solubility allows it to dissolve into the groundwater in “pulses” that result in rapid order-of-

magnitude changes in groundwater concentrations; pulses, which may be caused by rainwater infiltration or rising groundwater levels, may necessitate frequent groundwater sampling to determine actual MTBE concentrations and levels of risk to downgradient receptors; sampling frequency should be based on groundwater velocity and number of monitoring wells; determining the impact of selected remediation methods may be difficult without accurate historical sampling data

Transport of MTBE

- MTBE moves in groundwater almost at the same velocity as the recharge water
- downward velocity and travel times of recharge water to the water table are extremely variable throughout the United States, depending on
 - precipitation
 - evapotranspiration
 - unsaturated zone hydraulic conductivity
 - unsaturated zone thickness
- where depth to the water table is shallow, and the unsaturated zone is permeable, recharge from precipitation can reach an aquifer in days
- once in the groundwater, MTBE has a retardation factor of nearly 1; thus, it moves about the same rate as groundwater in all directions

Volatility and air concentration

- in the atmosphere, the half-life of MTBE can be as short as three days in a regional airshed (this is a physical mixing half-life, not the chemical or biological decay half-life); washout of gas-phase MTBE by precipitation would not, by itself, greatly alter the gas-phase concentration of MTBE in air
- MTBE partitioning to precipitation, equilibrium solubility, is 3 µg/L or more MTBE to surface or groundwater
- MTBE concentrations in urban air are on the order of 1 ppb by volume or less
- when moving from the liquid phase (i.e., free product) to the vapor phase, MTBE is three times more volatile than benzene (i.e., the vapor pressure of MTBE is three times the vapor pressure for benzene)
- when moving from the dissolved phase (in water) to the vapor phase, MTBE is about 10 times less volatile than benzene, i.e., its Henry's law constant is $1/10$ of benzene's
- although MTBE can volatilize from water, half-lives (physical mixing half life) in rivers and streams can be greater than 1 day; before half of the MTBE is volatilized, travel distances range from 0.8 km for shallow streams to more than 900 km for deep rivers
- ice on rivers and streams will stop MTBE volatilization from water
- factors that influence volatilization of MTBE in surface water include velocity, depth, and temperature of water; wind speed; air temperature; and sometimes depth and

flow velocity. In deep, slow-moving flows, MTBE volatilizes at rates similar to those for BTEX compounds; in shallow, slow-moving flows, MTBE volatilizes at rates significantly slower than for BTEX compounds

On the issue of biodegradability

- MTBE is much more resistant to biodegradation than benzene
- MTBE is generally reported as recalcitrant, therefore no widely accepted estimates of its biochemical decay half-life exist
- MTBE is recalcitrant in anaerobic laboratory studies under the following conditions:
 - denitrifying
 - Fe(III) or iron-reducing
 - sulfate-reducing
 - methanogenic-reducing
 - anaerobic
- in an aerobic study, after more than 100 days of incubation, no MTBE degradation was found
- significant aerobic MTBE degradation has been observed in stream-based sediments (Bradley and others, in press)

- MTBE degradation, nevertheless, has been reported (see *UTTU* article on "MTBE biodegradation studies")
- degradation of MTBE can potentially lead to the formation of tert-butyl alcohol, which can cause carcinogenic activity in laboratory animals (Reviewer's note: *TBA can also originate from fuel spills, thus the presence of TBA is not necessarily evidence for MTBE biodegradation.*)

References

Lucas, G., "Davis Moves to Phase-Out MTBE Additive: Oil Industry to Hear Governor's Plan Today," *Chronicle*, Sacramento Bureau, March 25, 1999; <http://www.sfgate.com/cgi-bin/article.cgi?file=/chronicle/archive/1999/03/25/MN82915.DTL>.

Reiser, G. and A.K. O'Brien, "Occurrence and Seasonal Variability of Volatile Organic Compounds in Seven New Jersey Streams," May 1998, U.S. Geological Survey, U.S.G.S. Branch of Information Services, Box 25286, Building 810, Denver, Colorado 80225-0286; <http://wwwrvares.er.usgs.gov/nawqa/>.

Squillance, P.J., Pankow, J.F., Korte, N.E. and J.S. Zogorski, "Environmental Behavior and Fate of Methyl tert-Butyl Ether (MTBE)," February 1998, U.S. Department of the Interior, U.S. Geological Survey, National Water Quality Assessment Program; <http://wwwrvares.er.usgs.gov/nawqa/>.

Definition of MTBE terms

Following are definitions of terms related to MTBE usage in the United States.

Clean Air Act of 1990 Congress mandated the use of reformulated gasoline (RFG) in areas of the country with the worst ozone or smog problems. RFG must meet certain technical specifications set forth in the Clean Air Act, including a specific oxygen content. Ethanol and MTBE are the primary oxygenates used to meet the oxygen content requirement. MTBE is used in about 84 percent of the RFG supplies. Currently 32 areas in a total of 18 states participate in RFG programs. RFG accounts for about 30 percent of gasoline nationwide.

Federal reformulated gasoline Gasoline mandated by federal law, which must contain a certain percentage of oxygen content in non-attainment areas. In compari-

son to conventional gasoline, RFG shows significant improvement on several measures of air quality such as reduced emissions of carbon monoxide, volatile organic compounds and nitrogen oxides. Conventional gasoline refers to gasoline used nationwide before 1995.

Health advisory Non-mandatory standards for action that are used only for guidance and are not legally enforceable. They are subject to revision as new information becomes available. The U.S. EPA health advisory on MTBE in 1998 stated that drinking water containing maximum concentrations of 20 to 40 µg/L (ppb) would likely not create water with unpleasant taste and odor for most people.

MTBE, Methyl tertiary-butyl ether See the article "General information on MTBE."

Oxyfuels Oxygenated fuels that contain oxygenates at concentrations on the order of 10 to 15 percent by

volume. They are used in urban areas during winter months to help reduce automotive CO emissions that deteriorate air quality. The Federal Clean Air Act Amendments of 1990 (CAAA) mandated the use of oxygenated fuels during winter months in approximately 40 urban areas throughout the United States that did not meet ambient CO standards. In these designated "non-attainment" areas, gasoline sold in the winter months must contain at least 2.7 percent by weight (wt percent) oxygen, effective November 1992.

Oxygenates Organic molecules that contain oxygen. They are typically alcohols such as ethanol, or ethers such as MTBE. Adding oxygenates to fuels promotes more efficient combustion under adverse conditions in the engine, such as cold starts or fuel-rich operations. The extra oxygen helps convert carbon monoxide, (CO, a product

U.S. EPA, "Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on Methyl Tertiary-Butyl Ether (MTBE)," December 1997, Fact Sheet, EPA-822-F-97-009; <http://www.epa.gov/OUST/mtbe>.

U.S. EPA, "MTBE Overview," January 1998, Fact Sheet # 1, EPA-510-F-97-014, <http://www.epa.gov/OUST/mtbe>.

U.S. EPA, "Remediation of MTBE Contaminated Soil and Groundwater," January 1998, Fact Sheet # 2, EPA 510-F-97-015; <http://www.epa.gov/OUST/mtbe>.

U.S. EPA, "Use and Distribution of MTBE and Ethanol," January 1998, Fact Sheet # 3, EPA-510-F-97-016; <http://www.epa.gov/OUST/mtbe>.

Zogorski, J.S., Morduchowitz, A., Baehr, A.L., Bauman, B.J., Conrad, D.L., Drew, R.T., Korte, N.E., Lapham, W.W., Pankow, J.F. and E.R. Washington, "Fuel Oxygenates and Water Quality: Current Understanding of Sources, Occurrence in Natural Waters, Environmental Behavior, Fate and Significance," October 1996; Office of Science and Technology Policy, Executive Office of the President, Washington D.C. 20500, or contact John Zogorski, 605-394-1780, extension 214, fax 605-394-5373, e-mail, jszogors@usgs.gov.



The Borden MTBE plume study

Schirmer and Barker (1998) investigated an MTBE plume approximately eight years after researchers injected, below the water table, groundwater containing dissolved oxygenated (MTBE) gasoline with a chloride (Cl⁻) conservative tracer. This field experiment took place at the Canadian Forces Base Borden Aquifer. Researchers wanted to characterize MTBE distribution in the aquifer and perform a reliable mass balance on the MTBE. They used numerical and analytical models and geostatistical methods for the design of the sampling grid and for result analysis.

Aquifer characterization

Characteristics of the well-studied Borden Aquifer include:

- a well-defined hydraulic conductivity field
- an underlying, extensive regional clayey and sandy silt aquitard, which is about 8 m thick at the field site
(*Reviewer's note: this aquitard is not strictly impermeable*)
- mean groundwater velocity of 33 m/year

Definition of MTBE terms (continued)

carbon dioxide. To a lesser extent, the oxygen may help convert hydrocarbons to carbon dioxide and water. MTBE, the most common fuel oxygenate, is used in more than 80 percent of the oxygenated fuels. Ethanol, the second most common fuel oxygenate, is used in about 15 percent of the oxygenated fuels. Other oxygenates, which constitute the remaining 5 percent of the market, include tertiary amyl methyl ether (TAME), ethyl tertiary butyl ether (ETBE), di-isopropyl ether (DIPE) and tertiary butyl alcohol (TBA). For more information on ethanol, see the U.S. EPA Fact Sheet # 3.

Reformulated gasoline RFG was developed to reduce automotive pollutant formation, especially evaporative emissions and exhaust emissions of photochemical ozone

precursors. The most important targeted zone precursors are volatile organic compounds. RFG also intended to reduce air toxic emissions of benzene, 1,3-butadiene, formaldehyde and acetaldehyde.

Tert-butyl alcohol TBA is a possible degradation intermediate of MTBE and a primary MTBE human metabolite along with formaldehyde. It is also an oxygenate.

Tert-butyl formate TBF is an important combustion by-product of MTBE at ambient temperatures, but not at elevated temperatures.

Toxicokinetics The quantitative study of how a substance is taken up, distributed to internal organs, metabolized and eliminated from the body.

References

Keller, A., Froines, J., Koshland, C., Reuter, J., Suffet, I. and J. Last, *Health & Environmental Assessment of MTBE: Report of the Governor and Legislature of the State of California as sponsored by SB 521, Vol. 1, Summary & Recommendations*, November 1998; <http://www.tsrtpt.ucdavis.edu/mtberpt/vol1.pdf>.

U.S. EPA, "Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on Methyl Tertiary-Butyl Ether (MTBE)," Fact Sheet, EPA-822-F-97-009, December 1997, <http://www.epa.gov/OUST/mtbe>.

U.S. EPA, "MTBE Overview," Fact Sheet # 1, EPA-510-F-97-014, January 1998, <http://www.epa.gov/OUST/mtbe>.

U.S. EPA, "Remediation of MTBE Contaminated Soil and Groundwater," Fact Sheet # 2, EPA 510-F-97-015, January 1998; <http://www.epa.gov/OUST/mtbe>.

U.S. EPA, "Use and Distribution of MTBE and Ethanol," Fact Sheet # 3, EPA-510-F-97-016, January 1998, <http://www.epa.gov/OUST/mtbe>.

- groundwater that flows northward, with seasonal fluctuations of about 20 degrees
- a relatively low carbon content of 0.02 percent, and thus a low sorption capacity for organic compounds
- homogeneity

Background

In 1988, workers injected about 2,800 liters of groundwater 1.5 m below the water table. The groundwater was spiked with

- Cl^- (448 mg/L)
- gasoline-derived organics (including about 19 mg/L BTEX)
- MTBE (269 mg/L)

This slug moved downgradient at about 33 m/year (110 ft/year) under natural gradient conditions. Researchers constructed a dense network of multilevel piezometers, typically using 14 depth points over a 2.8 to 4.2 m vertical zone, to monitor contaminants. They sampled the groundwater at days 6, 42, 106, 317, 398 and 476. They found that the BTEX compounds rapidly biodegraded (aerobically) and were almost completely attenuated during the initial 16-month (476-day) period.

The mass ratio MTBE/ Cl^- initially was 0.59 and remained so until day 476 when the ratio decreased to 0.43. "The MTBE/ Cl^- concentration ratios for single samples ranged from 0.33 to 1.0 for the initial 476 days of the experiment. Due to the uncertainty of the field mass balance estimates, MTBE degradation could not be demonstrated and it was concluded at the time that the compound was either persistent during the 16 months of monitoring or degrading at a rate not detectable under the experimental conditions" (Schirmer and Barker, 1998). (Reviewer's note: No appreciable bioattenuation was found during the study's first 16 months.)

In 1995 and 1996, 7 to 8 years later, researchers took additional samples to locate and characterize the MTBE plume (Figure 1). In their paper Schirmer and Barker (1998) discuss in detail the sampling plan. Basically three sampling rounds were conducted: Nov. 1995, Jul/Aug 1996, and Nov. 1996.

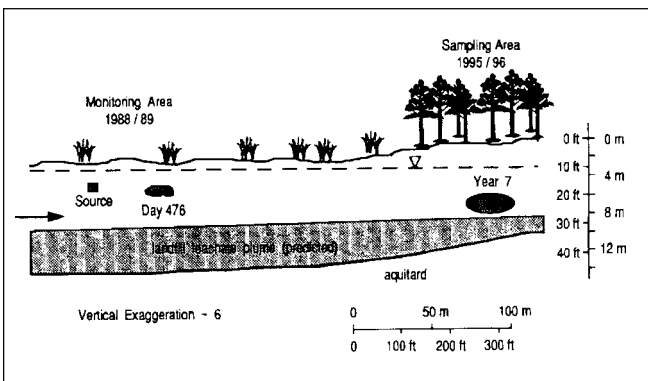


Figure 1. Source, plume location after day 476 and anticipated location after 7 years (from Schirmer and Barker, 1998, used with permission from NGWA).

Analytical modeling and numerical simulations

Researchers used the 3-dimensional model SLUG3D to estimate MTBE plume location. The program simulates 3D advective/dispersive transport in a homogeneous aquifer. The modeling indicated "MTBE peak concentrations of more than 3,000 $\mu\text{g/L}$ and movement of the plume 240 m beyond the injection site. A slight downward movement of the MTBE plume over the initial 476 days of observation indicated there was probably recharge on top of the aquifer, which the model does not consider" (Schirmer and Barker, 1998).

Researchers also performed numerical simulations using random hydraulic conductivity (K) fields. They found the transverse (both vertical and horizontal) dispersion of contaminants to be minimal, which was consistent during the first 476 days of the experiment. Thus, only minor additional vertical spreading of the MTBE plume would be expected after sampling in 1989 (day 476).

Researchers predicted the locations of "three plumes determined with the numerical model using different random K fields. The three realizations give insight into the uncertainty of the location of the remaining MTBE even in this well-studied and relatively homogeneous aquifer. The plume development of all generated plumes was compared to the results of the initial 16 months of the experiment." Researchers found agreement between "a modeled and field-observed plume" (Schirmer and Barker 1998).

After field sampling, workers took soil cores and analyzed them for hydraulic conductivity to ensure that "the assumed statistical properties for the numerical flow and transport modeling held for the entire aquifer." They found this to be true. In addition, examination of the hydraulic properties of the aquitard indicated that any flux from the aquifer into the aquitard would be extremely small. (Reviewer's note: This flux, however, would be significant for vertical migration of MTBE combined with infiltration).

Sampling

As mentioned earlier, researchers sampled three times after the 7-year period. The first, in November 1995, involved 13 locations, three to four samples taken at each with a vertical spacing of 1.5 m. Researchers detected MTBE at six locations with a maximum concentration of 343 mg/m^2 . These concentrations were lower than modeling predicted. Researchers found the plume length, but not its longitudinal extent.

For the second sampling round, July/August 1996, researchers wanted to "design an optimal sampling grid with a minimal number of sampling locations while assuring that the plume was delineated in enough detail so that a reliable MTBE mass could be calculated." They used statistical methods to define optimal grid spacing. This coarse grid covered a 100 m by 40 m area and had 30 sampling locations spaced 20 m apart longitudinally and 10 m apart transversely. Each location had four to eight sampling points distributed vertically at each location with 0.25 to 1.0 m spacing.

To date, the data indicate no slow-moving slug with high MTBE concentrations. (*Reviewer's note: Again, the reader should be cautioned that there is extreme uncertainty that this model does not account for. The model is simple and its assumptions have some flaws.*)

Mass estimation

Researchers used KRIGING routine with GRIDVOL to determine mass of recovered total MTBE, which was 22 g. Another method gave 24.5 g. The mass of MTBE introduced into the aquifer was 752 g. This agrees with previous determinations that only 3 percent of the initial MTBE mass was found.

Conclusions

From this study of the Borden Aquifer, researchers concluded:

- the MTBE plume location was in good agreement with the location suggested by numerical modeling—during the first 16 months
- MTBE concentrations were more than an order of magnitude lower than expected, based on numerical modeling; modeling considered dispersion and diffusion as the only attenuation mechanisms (*Reviewer's note: the discrepancy may have resulted from using a poor model, weak assumptions and flawed input variables.*)
- MTBE was present only in the deepest portion of the aquifer, near the aquitard; this suggests that the dilute anaerobic landfill leachate present mixed with the MTBE plume, creating conditions amenable to persistence of the MTBE (*Reviewer's note: this suggests vertical movement was very important.*)
- the lower calculated MTBE/Cl⁻ ratios after the first 16 months of the experiment suggest that the MTBE had undergone transformation or that additional Cl⁻ from other sources, such as the landfill leachate plume, had mixed with the plume
- neither TBA nor TBF, two potential MTBE degradation products, were found in any samples; this suggests either that MTBE had not biodegraded or that the degradation products further transformed and were not detected
- in general, non-detect levels of MTBE were found at the peripheries of the sampling grid
- the mass balance results suggest a significant loss of MTBE, potentially attributable to
 - biodegradation
 - abiotic degradation
 - volatilization
 - plant uptake
 - sorption

Researchers discounted all of the above except biodegradation. Because the aquifer was so well-characterized and the MTBE appeared where models suggested, Schirmer and Barker believe that they did not "miss" the plume; they propose that biodegradation is responsible for the mass difference of initial and final MTBE. "Nevertheless, additional lines of evidence of biodegradation, such as laboratory batch and column experiments, are necessary to confirm this possibility. Studies are underway, but no confirmatory laboratory evidence has been found to date. **Thus, while we are confident that MTBE mass has been lost, we cannot yet confirm biodegradation as the process . . .** Research is now needed to determine which types of subsurface environments do support MTBE biodegradation, and to define the microbiological and geochemical factors that influence MTBE biodegradation. This understanding is necessary before biodegradation can be considered for intrinsic remediation of MTBE in groundwater" (*Schirmer and Barker, 1998*).

Reviewer's note: The model used to predict the MTBE fate and transport was deterministic and not stochastic, and the model's assumptions are not strong. Was uncertainty incorporated into the model? The reader should be aware that this study is considered by some to be very controversial. The MTBE that "might" have biodegraded could actually have vertically dispersed through the lower aquitard. Other unanswered questions include: how was bio-decay considered in the model? Was phytoremediation significant? What about MTBE movement through the aquitard from the combined effects of vertical flow and infiltration?

Reference

Schirmer, M. and J.F. Barker, "A Study of Long-Term MTBE Attenuation in the Borden Aquifer, Ontario, Canada," Spring 1998, *Ground Water Monitoring and Remediation*; 800-332-2104; <http://www.ngwa.org>.

UTTU thanks Dr. Jim Barker, University of Waterloo, Department of Earth Sciences, for his help on this article.



MTBE study at the U.S.G.S. site in South Carolina

Scientists gathered data concerning the fate of MTBE (methyl tert-butyl ether) in a shallow sandy aquifer over a period of 6 years. They monitored the MTBE using both monitoring wells and multilevel sampling wells (MLS) and performed laboratory microcosm studies to better define MTBE's biodegradation potential. Scientists found a "low but measurable biodegradation potential (<3 percent ^{14}C -MTBE as $^{14}\text{CO}_2$) after a seven-month incubation period" (Landmeyer and others, 1998).

Historical perspective on MTBE

Because MTBE has been used as a fuel oxygenate only since the late 1970s, little time-series field data exist describing the behavior of MTBE compared to the BTEX compounds (benzene, toluene, ethylbenzene and xylenes). The Landmeyer and others (1998) study (1993 to 1998) is different in this respect, and "documents the long-term spatial distribution of MTBE and benzene at a point-source gasoline-spill site containing fuel oxygenates."

Of special interest is the question of MTBE biodegradation. A proposed microbial-MTBE transformation intermediate is tert-butyl alcohol, TBA, which was detected in MTBE-contaminated wells. TBA, however, was also detected in unsaturated release-area sediments, suggesting that TBA may have been present in the fuel that was originally released. Another potential MTBE transformation intermediate is tert-butyl formate (TBF).

Spill history and study area

The study area is located in the Atlantic coastal plain and geophysical province in South Carolina. In September 1991, workers detected gasoline containing fuel oxygenates in a shallow aquifer. The source, a gasoline station UST, had likely begun leaking fuel in the mid-1980s. A remedial investigation in 1993 indicated BTEX concentrations were approaching the maximum contaminant levels (MCLs). In October 1993, workers excavated the UST and surrounding sediments. In 1994, several government agencies assessed BTEX fate and transport using a numerical solute-transport model.

The aquifer under study has these characteristics:

- shallow and unconfined
- comprised of silty, well-sorted sand grains of Pleistocene to Holocene age to a depth of about 45 feet
- underlain at about 45 feet by a regional clay-rich confining unit
- an average depth to water of 13 feet near the source area
- an average depth to water of 2 to 9 feet near a concrete-lined drainage ditch, about 700 feet from the source area
- an average hydraulic conductivity of 11 ft/d and an average groundwater flow rate of 70 ft/yr near the source area; near the concrete-lined ditch, average groundwater flow is up to 500 ft/yr
- recharge by rainwater infiltration of about 20 to 25 in/yr
- water level fluctuations from 2 to 3 feet (depicted in two wells) over the 1993 to 1998 sampling period
- where the silty sand is uncontaminated, grains have a ferric oxyhydroxide coating, consistent with a measured dissolved oxygen content of 4 mg/L (i.e., originally an aerobic aquifer)

Field sampling discussion and results

Workers collected groundwater samples from 1993 to 1998, using monitoring wells and multilevel sampling wells (MLS) to give areal and vertical distributions of MTBE and BTEX. Workers also measured these dissolved species/elements:

- H_2
- Fe(II)
- sulfide
- sulfate
- CH_4
- oxygen concentrations

The sampling procedures and analytical methods used are more fully described in the text.

Landmeyer and others (1998) defined the extent of MTBE contamination by the 20 $\mu\text{g/L}$ isoconcentration contour. Sampling results indicated the following:

- in April 1993, the 20 $\mu\text{g/L}$ MTBE contour had migrated about 330 feet in the direction of groundwater flow from the source area; because 70 ft/yr is the rate of groundwater advection, scientists believe the fuel release occurred as early as 1988 (*Reviewer's note: 70 ft/yr is about 21 m/yr; in the previous article on the Borden Aquifer, groundwater velocity was 1.5 times greater or 33 m/yr.*)
 - the 5 $\mu\text{g/L}$ benzene contour migrated only about 270 feet, or roughly 80 percent of the distance MTBE migrated; this is consistent with benzene's retardation factor, and MTBE's higher solubility, lower adsorption and biodegradation potential under anaerobic conditions
 - by March 1994, the 20 $\mu\text{g/L}$ MTBE contour extended another 100 feet; the 5 $\mu\text{g/L}$ benzene contour also extended to this distance
 - in June 1996:
 - MTBE concentrations of 18 and 1 mg/L measured in the farthest downgradient well resulted from the well intercepting "converging shallow and deep groundwater flow lines that had originated near the release area; here there was an order of magnitude increase in groundwater flow rates. . ."
- (Landmeyer and others, 1998)

- in the area of the water table aquifer where flow rates are 70 ft/yr, the areal distribution of MTBE and benzene reflects both lateral and transverse dispersion tendencies
- the 10,000 µg/L MTBE contour had migrated about 75 feet from the source area
- In January 1997:
 - MTBE and benzene were still being measured in the furthest downgradient well
 - the upgradient edge of the 10,000 µg/L MTBE contour was displaced 100 ft downgradient from its June 1996 position
 - MTBE concentrations in the plume center were two orders of magnitude lower compared to 1993 values
 - benzene did not show a similar downgradient movement of the 1,000 µg/L contour
- In July 1997:
 - sampling showed little change of MTBE and benzene concentrations, which may reflect lack of transport due to measured low water levels
- In January 1998:
 - MTBE and benzene distributions (20 and 5 µg/L) were similar to the July 1997 distributions
 - the 10,000 µg/L MTBE contour moved about 200 feet from the July 1997 location, resulting from increase in hydraulic gradients in the area and increased water levels due to above-normal rainfall
- because of the increase in recharge, the MTBE and benzene distribution widths near the release decreased, while the transverse distribution of the 20 µg/L MTBE contour increased near the discharge area

Vertical distribution of MTBE: diving plume

Landmeyer and others (1998) found higher MTBE and benzene concentrations in the MLS deeper sampling ports. "This observation of higher concentrations of light, nonaqueous-phase liquids (LNAPLs) at depth suggests that recharge is causing the dissolved-phase MTBE and benzene to be displaced deeper into the aquifer. The most extreme water table fluctuation observed over the study period was near 3 ft (0.9 m). . . representing about 0.9 x 10⁶ gallons of recharge."

The authors state that "It is also significant that the highest MTBE and benzene concentrations are not found near the surface of the water table, as would be expected from a LNAPL gasoline product floating on the water table, but rather nearer the center sampling ports of MLS. . . Again, this vertical distribution suggests recharge by rainwater infiltration is causing a vertical component of groundwater flow that moves both dissolved MTBE and benzene compounds deeper into the aquifer as the distance from the source area increases. This has important implications for the outcome of site remedial investigations, many of which, although containing wells downgradient from the source areas, have screens placed near the water table surface (rather

than at deeper depths where the plume could actually exist). Similar to the transverse dispersion shown in the areal plots, the vertical dispersion of MTBE in the aquifer nearer the source area is also about one-half the horizontal plume distribution."

Comparison of the January 1998 and June 1996 data showed that the upgradient limit of the 1,000 µg/L MTBE contour moved about 200 feet, while benzene concentration decreased by an order of magnitude. "The 5 µg/L contour line has been displaced deeper in the aquifer than measured in June 1996, as evidenced by the lack of benzene detection in shallower sampling ports that were contaminated in 1996" (Landmeyer and others 1998).

MTBE biodegradability: historical perspective and recent laboratory experiments

Most scientists believe that MTBE is not easily biodegraded under either aerobic or anaerobic conditions. Following are brief descriptions of MTBE biodegradation studies (complete references appear in Landmeyer and others, 1998):

- Mo and others, 1996, reported MTBE degradation achieved using acclimated enrichment cultures, under aerobic conditions, "a condition which tends to over-predict degradation processes that can be expected of natural microbial communities at most gasoline-contaminated sites"
- Park and Cowan, 1997, observed aerobic MTBE degradation with an unidentified mixed enrichment culture; degradation occurred only between 15° and 35°C
- Daniel, 1995, and Borden and others, 1997, observed TBA as an intermediate breakdown product of low concentrations of MTBE in microcosms containing gasoline-contaminated aquifer sediments; however, TBA production was not observed when MTBE concentration was greater than 1 mg/L
- several authors reported little evidence of MTBE biodegradation under nitrate-reducing, sulfate-reducing or methanogenic conditions
- Mormile and others, 1994, conducted a laboratory study using fuel-contaminated aquifer sediments incubated under anaerobic conditions; they found decreased MTBE related to stoichiometric increases in TBA concentration, but only in a single replicate after 152 days
- Hardison and others, 1997, showed MTBE can be co-metabolized in the presence of short-chain alkanes found in gasoline

(For more studies, see "MTBE biodegradation studies" in this issue of *UTTU*.)

In the Landmeyer and others (1998) study, scientists measured MTBE biodegradation potentials in the laboratory. They quantified ¹⁴CO₂ produced from a known amount of uniformly labeled ¹⁴C-MTBE that was added to microcosms containing aquifer material. "Treatments were comprised of triplicate 40-ml glass microcosms containing 5 ml of a slurry of water table aquifer material and groundwater. Dead controls

for the triplicate treatments were initially made sterile by autoclaving the control microcosms for 1 hour at 121°C, and maintained sterile for the duration of the experiment by addition of 8 millimolar (mM) HgCl₂. All incubations were conducted at room temperature (25°C) and in the dark" (*Landmeyer and others, 1998*).

Scientists designed the treatments to assess MTBE biodegradation potential based on

- MTBE concentration
- redox condition
- presence of alternative organic substrate

"To assess the effect of MTBE concentration on biodegradation potential, approximately 73,000 (low) to 666,000 (high) dpm (decays per minute) of ¹⁴C-MTBE were added to the microcosms. To observe differences in degradation based on redox conditions, aerobic (oxygen headspace) and anaerobic (helium headspace) treatments were created with identically prepared dead controls for both low and high MTBE concentration treatments. The anaerobic treatments were naturally Fe(III) reducing. To observe the effect of alternative organic substrates, such as BTEX compounds, on MTBE biodegradation potential, the above two treatments were set up with aquifer sediment from near well 8 that had both MTBE and BTEX, and with aquifer sediments from near well 16 that had MTBE and lower BTEX concentrations" (*Landmeyer and others, 1998*). At specified times, workers added phosphoric acid to the treatment vials and dead controls, converting the dissolved ¹⁴CO₂ to gas. This radioactivity was consequently measured in a scintillation counter.

Microcosms containing sediments near well 8 and 16 showed "low but measurable biodegradation potential (<3 percent ¹⁴C-MTBE as ¹⁴CO₂) under Fe(III)-reducing conditions. This was the total accumulation of CO₂ as a byproduct after a seven-month incubation period. There was no statistically significant difference in ¹⁴CO₂ production between the various treatments." Possibly, other intermediate biodegradation compounds were produced, but none were quantified in this study. Scientists believe the low biodegradation potentials and high rates of groundwater flow are responsible for the continued presence of tens of milligrams per liter of MTBE still existing in wells 700 feet from the release area.

Scientists did find TBA, a possible degradation intermediate of MTBE, up to 5 mg/L in some water samples between June 1996 and January 1998. Aquifer sediments, collected at the water table and above the unsaturated zone, were analyzed for MTBE, TBA and TBF. Scientists found the saturated sediments contained no measurable MTBE, TBA or TBF; however, the unsaturated sediments had MTBE (up to 6,272 µg/L), TBA (up to 397 µg/L) and no TBF. Landmeyer and others (1998) suggest "a possible explanation for this large difference in concentration across a small vertical distance is that the contaminated unsaturated-zone sediments are exposed to water only during recharge events, whereas the deeper sediments are continually flushed with clean groundwater originating from areas upgradient of the release. The lack of TBF in either saturated or unsaturated sediment can be explained by the rapid hydrolysis of TBF to TBA."

Conclusions

From this 6-year study of MTBE fate, researchers concluded the following:

- MTBE has the potential to be transported farther than benzene
- MTBE and benzene can migrate deeper than many conventional water-table well screens—a diving plume—and remain undetected
- MTBE may persist in groundwater systems because of low biodegradation potentials under the anaerobic conditions found in most gasoline-contaminated aquifers

"Although natural attenuation of contaminant compounds is usually demonstrated by evoking biodegradation processes that remove contaminant mass from a groundwater system, this study suggests that abiotic natural attenuation processes of dilution and dispersion in the direction of groundwater flow also play an important role in reducing MTBE concentrations."

Reference

Landmeyer, J.E., Chapelle, F.H., Bradley, P.M., Pankow, J.F., Church, C.D. and P.G. Tratnyek, "Fate of MTBE Relative to Benzene in a Gasoline-Contaminated Aquifer (1993-98)," 1998, *Ground Water Monitoring & Remediation*, Spring 1998; 614-898-7791; GWPC@ngwa.org

UTTU thanks Dr. Jim Landmeyer for his help on this article.



MTBE/BTEX plume evolution as determined by three sampling events

MTBE came into use in the Long Island area of New York in the late 1970s as an octane enhancer. Use in gasoline at that time was in the range of 5 to 15 percent by volume. In East Patchogue in the mid 1980s, workers discovered subsurface contamination in a residential well. They drilled monitoring wells upgradient and downgradient to locate the source, which happened to be an abandoned service station approximately 1,200 m upgradient (Weaver and others, 1996).

Site history and sampling events

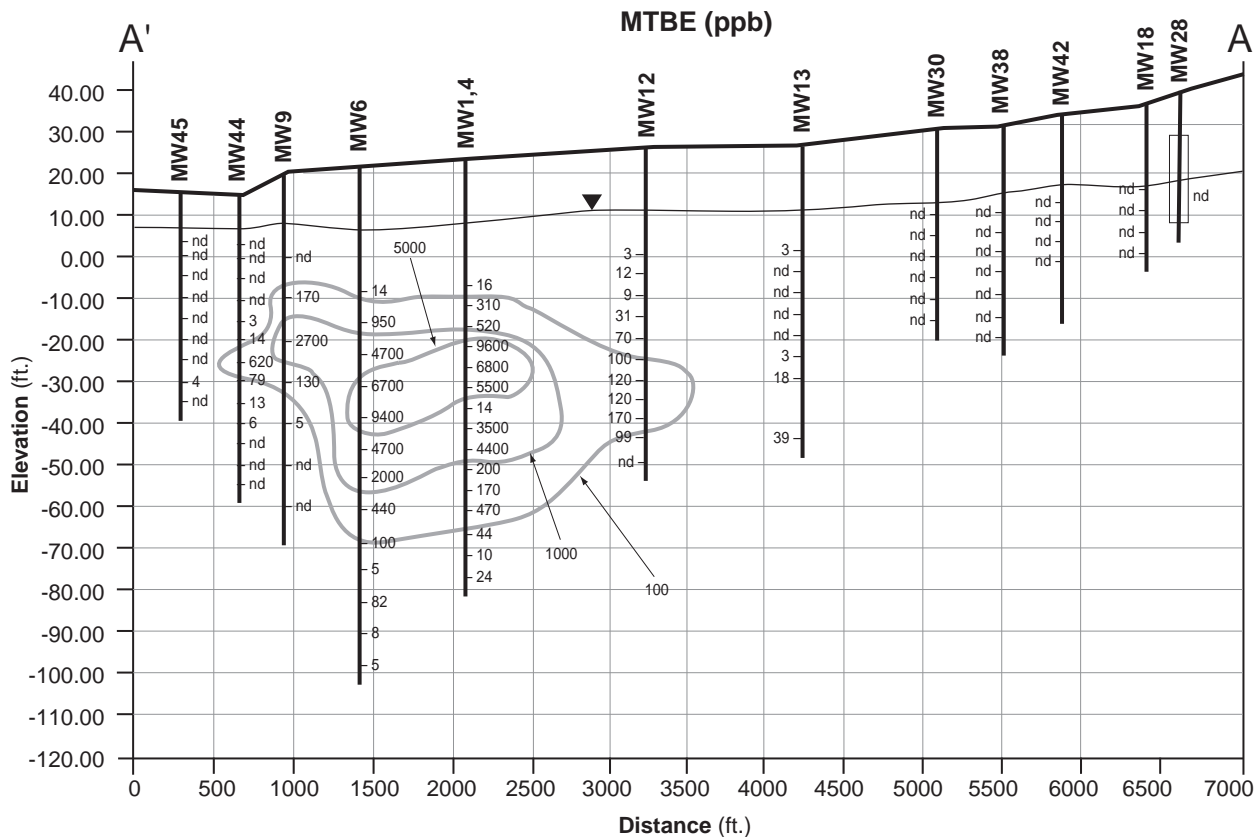
After discovering the contamination, workers drilled soil borings around the source to confirm the presence of hydrocarbon contamination. Apparently the station's tanks were removed in 1988. In 1994 and 1995 workers mapped the contaminant plume using samples from 26 multilevel samplers and 22 monitoring wells. Weaver and others (1996) analyzed groundwater from three sampling events for BTEX

and MTBE. The sampling events, roughly six months apart, occurred in December 1994, April 1995, and October 1995. The large number of samples generated a three-dimensional data set that was used to calculate moments of concentration distribution—a procedure outlined in Weaver and others (1996).

Contaminant concentrations

Researchers found that "the estimated mass of benzene, toluene, ethyl-benzene and xylenes decreased between each sample round. Each of these compounds is expected to undergo biodegradation in the aquifer, but each continued to dissolve into the aquifer through October 1995. The latter fact is established by the persistence of BTEX concentrations near the source. The mass of MTBE, however, appeared to increase between the first two sample rounds, then decrease between the second and third sample rounds. The distribution of MTBE was such that in all sample rounds, no MTBE was found between the source and a point approximately 600 m downgradient. Thus it appears that the MTBE was almost entirely leached from the gasoline near the source" (Weaver and others, 1996). Table 1 shows MTBE and BTEX concentrations calculated from pore volume estimates and measured concentrations in the sampling network where concentrations were above non-detect.

Figure 6. MTBE distribution as depicted by the April 1995 sampling event (Weaver and others, 1996).



volume. The average MTBE concentration would be expected to decrease, which it does not" (*Weaver and others, 1996*).

From sample round two to three, the mass centers of both the ethyl benzene and xylenes retreated, suggesting that the rate of input of mass of these compounds to the aquifer is less than the rate of their loss (*Weaver and others, 1996*).

Conclusions

Although researchers did not know exactly when the releases occurred, they were able to determine contaminant mass, whose accuracy was dependent on

- an extensive monitoring network; note that vertical sample spacing (Figures 6 and 7) is 5 to 10 feet
- duration of sampling events
- accuracy of the procedure used for making estimates

Researchers also documented a BTEX mass decrease over the three sampling rounds; MTBE, however, did not show such a clear trend.

In addition, researchers learned that "Vertical delineation is extremely important in tracking dissolved contaminants. It has been observed that infiltration of precipitation/rainwater creates a loading mechanism that layers clean water on top of contaminated water. . . . If the average rainfall for New York is 41 in/yr, and it is assumed that the entire column infiltrates [into the subsurface], the plume will be layered by 3.5 feet of clean water. Over the course of 10 years, the plume could be layered by 35 feet of clean water. (Porosity effects would have to be factored into this analysis.) Based on this theory, all monitoring wells that were of standard construction would not have detected the plume at a certain distance away from the source. Depending on the formation's characteristics, a 10-foot vertical sampling interval could miss contamination. We feel much more confident with our results using 5-foot sampling intervals" (*Reardon, 1999*).

"In addition, Long Island has very large hydraulic conductivity values and smaller gradients; areas of lower hydraulic conductivity and higher gradients may have deeper plumes based on shorter distance traveled but would have the same annual rainfall" (*Reardon, 1999*).

Current studies of the East Patchogue plume involve delineation of plume length. Results will be reported in a future issue of *UTTU*.

References

- Reardon, D., J.N.M. Environmental, personal communication, April 6, 1999.
- Weaver, J.W., Haas, J.E. and J.T. Wilson, "Analysis of the Gasoline Spill at East Patchogue, New York," *American Society of Civil Engineers Conference on Non-aqueous Phase*

Liquids in the Subsurface Environment: Assessment and Remediation, November 12-14, 1996, Washington D.C. <http://www.epa.gov/ada/patchogue.html>.

UTTU thanks David Reardon (JNMEnviro@aol.com), J.N.M. Environmental, Patchogue, New York, for his help on this article.



Diving plume in Kansas

Regulators recently discovered MTBE in two public supply wells in a small Kansas community. The plume, created by releases from three gasoline stations, had concentrations of up to 77,000 µg/L near the source. Although MTBE migrated beneath a line of monitoring wells, remediators were able to discover this plume by installing deeper monitoring wells. Hattan and Blackburn (*1999*) reported that "A deep monitoring well encountered an MTBE concentration of 1,600 µg/L located near a shallow monitoring well that produced a MTBE concentration of 5 µg/L."

By virtue of MTBE's specific gravity (0.740), which is less than water's, MTBE should be found near the top of the aquifer. MTBE was found at the aquifer's top near the source, but it penetrated to the aquifer's base where higher permeability materials existed. According to Hattan and Blackburn (*1999*) "The high solubility of MTBE enabled it to move rapidly through the groundwater, resulting in large plumes that follow the natural or induced groundwater gradient. Unlike BTEX plumes that radiate downgradient from the source area and stabilize within a few hundred feet, MTBE has been documented to extend over one mile downgradient from the source area. An important factor to consider when addressing MTBE sites is not to rely too heavily on shallow monitoring wells especially where deeper, more permeable zones could act as a migration pathway. Since this portion of the aquifer is typically utilized for public and private water wells, there should be increased concern."

Reference

- Hattan, G. and G. Blackburn, "Findings of Kansas MTBE Investigations," *Association of State and Territorial MTBE Workgroup Newsletter*, Vol. 2, No. 1, January 1999; 202-624-5828, <http://www.astswmo.org/Publications/summaries.htm#MTBE>.



Human health effects of MTBE

This article, summarized primarily from Keller and others (1998), describes the health effects of MTBE exposure with respect to taste and odor, toxicokinetics, acute symptoms, neurotoxicity, asthma, and reproduction.

Taste and odor

MTBE is said to have a taste that is "objectionable," "bitter", "solvent-like" and "nauseating." Sensitivity to MTBE varied widely, ranging from 2.5 µg/L to 680 µg/L (taste) and 2 µg/L to 190 µg/L (odor). Thresholds depend on the following:

- individual tested
- population tested
- water chlorination
- water temperature

"The California Department of Health Services proposed a secondary maximum contaminant level (SMCL) for MTBE of 5 ppb, based on available data of the observable detection thresholds. The SMCL is not set to protect against human health effects but rather to maintain the integrity of the aesthetic properties of drinking water and to ensure public confidence in water for drinking and cooking use" (Keller and others, 1998).

Toxicokinetics of MTBE

"Toxicokinetics is the quantitative study of how a substance is taken up, distributed to internal organs, metabolized and eliminated from the body" (Keller and others, 1998).

Studies of MTBE toxicokinetics have shown the following:

- upon inhalation, MTBE appears rapidly in the bloodstream
- MTBE is distributed to the liver, kidney and brain (animal studies)
- MTBE metabolism occurs in the liver, although the extent to which MTBE could be metabolized in other tissues has not been adequately investigated
- the primary metabolites formed are TBA and formaldehyde
- blood levels of TBA continue to increase for several hours after cessation of MTBE exposure
- the half-life of MTBE is about 1 hour
- metabolic clearance is slightly greater than exhalatory clearance
- the half-life of TBE is up to 10 hours (human studies)
- after exposure to small quantities of MTBE, MTBE and TBA are found in the urine of humans and animals, yet a large fraction of this MTBE is not accounted for in breath or urine of humans
- in animals, the majority of urinary eliminations from exposure to MTBE create TBE which, with further metabolic processing, creates alpha-hydroxyisobutyric acid and 2-methyl-1,2 propane diol

- small amounts of acetone have also been detected in rat urine
- further information is needed to confirm that the metabolites produced in rats are similar to those produced in humans
- studies of gallstones suggest MTBE may concentrate in human adipose tissue
- one human study (two subjects) suggests that up to 9 percent of inhaled MTBE may be retained in the lung's mucous membranes
- preliminary data suggest diversity in production and clearance of MTBE
- quantitative insights into human metabolic variability are likely only to come from studies of human specimens
- excess lymphomas and leukemias in rats resulted from MTBE exposure; however, assessing the implications for human risk will require additional research

Other questions raised regarding MTBE toxicokinetics are:

- what is the extent to which MTBE absorption occurs via oral ingestion and dermal uptake?
- is MTBE distributed to muscle and male gonads?

Acute effects of MTBE

Acute effects of MTBE exposure include

- noticeable odor
- headache
- nausea or vomiting
- burning sensations in the nose or mouth, coughing, dizziness, spaciness or disorientation or eye irritation

Since the symptoms are non-specific and anecdotal, their significance is difficult to interpret; however, they should not be dismissed merely because they cannot be explained.

Impact on asthma

No studies have been designed or carried out to determine if MTBE could exacerbate or cause asthma. "There have been no studies designed to evaluate respiratory sensitization from MTBE, and no published clinical reports were identified that document respiratory sensitization to MTBE itself. Therefore, there is little evidence at present, either to implicate or to exonerate MTBE as a cause or exacerbating factor in asthma. . . Evidence from epidemiologic studies suggests that residential proximity to streets with heavy traffic is associated with increased prevalence or activity of asthma in children. . . Chamber studies in which asthma patients who believe their illness is exacerbated by MTBE are exposed to MTBE or to MTBE blended with gasoline could help verify anecdotal reports. Because formaldehyde, a combustion byproduct of MTBE, may exacerbate and perhaps cause asthma, there is a plausible mechanism for the use of MTBE in gasoline to contribute to (perhaps small) increases in asthma incidence or severity. TBA is a skin sensitizer and could also be capable of causing or exacerbating asthma in sensitive individuals" (Keller and others, 1998).

Neurotoxicity

"A few studies have indicated that MTBE has the potential for producing effects associated with CNS (central nervous system) depression, including headache, dizziness, spaciness, nausea and disorientation. These effects appear to be reversible on cessation of exposure" (*Keller and others, 1998*). One study of 101 Finnish male road tanker drivers indicated that "drivers with longer periods of exposure to gasoline (containing 10 percent MTBE) scored higher for fatigue and hostility changes compared to those with shorter exposure. Additionally, 20 percent of the tanker drivers reported the following symptoms during the week (in order of decreasing frequency): headache, nausea, increased salivation, dizziness and dyspnea. This is the only known study designed specifically to measure CNS symptoms among occupationally exposed workers; however, in the absence of data on MTBE blood levels in these workers, it is not possible to determine the dose required to cause the effects observed" (*Keller and others, 1998*).

Humans exposed to high doses of MTBE seem to experience neurotoxic effects, such as sedation; however, the effects are reversible when exposure ends. Very high doses can cause ataxia, loss of righting reflex, tremors and labored breathing, but again, the effects are reversible when exposure ceases.

Reproductive and developmental studies

Keller and others (*1998*) were unable to find any human studies or case reports that evaluated the reproductive or developmental toxicity of MTBE. Experiments with laboratory animals have shown that exposure of MTBE at high levels (2,500 ppm or greater for 6 hours per day throughout gestation) caused maternal and fetal damage. MTBE may function as an endocrine disruptor in rodents, but the relevance of these findings has yet to be determined.

Epidemiological investigations of formaldehyde exposure and potential reproductive toxicity have produced contradictory results. "There is no evidence from reproductive toxicity studies of formaldehyde to suggest reproductive toxicity at doses less than those overwhelmingly toxic to the parent animals. . . . No human data were found regarding the developmental toxicity of tertiary-butyl alcohol (TBA)" (*Keller and others, 1998*). Ongoing rodent studies, however, are evaluating TBA's toxicity.

Carcinogenesis

"There are no human data on which an evaluation of the carcinogenicity of MTBE can be based. Substantial evidence from studies of chronic exposure by either oral or inhalation routes, however, demonstrated that MTBE is carcinogenic in rats and mice. Based on a thorough review of these carcinogenicity studies, supporting data on pathology and mechanisms of tumor induction, and carcinogenicity studies of MTBE's primary metabolites (TBA and formaldehyde), we conclude that MTBE is an animal carcinogen with potential to cause cancer in humans" (*Keller and others, 1998*).

"Further research is needed before we can reach a clear understanding of how MTBE causes cancer . . . The proposed mechanisms to explain the carcinogenic properties of MTBE are not adequately supported by currently available data. . . Our conclusion that MTBE is an animal carcinogen with the potential to cause cancer in humans is supported by several other comprehensive reviews of the literature" (*Keller and others, 1998*).

According to a report from the International Agency for Research on Cancer (IARC), however, MTBE is not classifiable as a human carcinogen (*OFA, 1998*). "Officially, IARC classified MTBE as a Group 3 chemical agent. According to IARC's classification system, a Group 3 chemical agent is defined as 'not classifiable to its carcinogenicity to humans.' Other agents officially classified as Group 3 compounds include . . . caffeine, tea, rubbing alcohol, talc and fluorescent lighting. . . A Group 3 compound is not classifiable as to its carcinogenicity to humans. Agents are placed in this category because of inadequate data in humans and inadequate or limited data in experimental animals. This group is used to describe agents which do not appropriately fall into any other group" (*OFA, 1998*).

"The IARC study follows by a year another European study that concluded 'MTBE is not carcinogenic according to the criteria (set forth in the European Union's) Directive on Dangerous Substances.' The earlier study, released by the European Centre for Ecotoxicology and Toxicology of Chemicals concluded that "the risk characterization for MTBE does not indicate concern for human health with regard to current occupational and consumer exposures'" (*OFA, 1998*).

The National Science and Technology Council 1997 Report (*Gestring and Anderson, 1998*) stated that "based on weight-of-evidence on MTBE carcinogenicity and considering various uncertainties, it is reasonable to regard this alkyl ether oxygenate as posing a potential carcinogenic hazard and risk to humans. At the same time, it should be recognized that the upper cancer unit risks for MTBE are similar to or slightly less than those for fully vaporized conventional gasoline, substantially less than benzene, a constituent of gasoline that is classified as a known human carcinogen, and more than 100 times less than 1,3-butadiene, a carcinogenic emission product of incomplete fuel combustion."

Reviewer's note: The Italian study by Belpoggi (reference found in Keller and others, 1998) found MTBE to be carcinogenic. This study, however, is controversial.

All of these studies indicate that at present, limited data exist for classifying MTBE as a human carcinogen. Human health studies on the effects of MTBE need to be completed.

Ecotoxicology

"Depending on time of exposure and endpoint measured, MTBE is acutely toxic to various aquatic organisms at concentrations from 44 mg/L to more than 1,000 mg/L in invertebrates. MTBE is acutely toxic to aquatic vertebrates at concentrations from 388 mg/L to more than 3,000 mg/L." Because the levels that indicate adverse effects are very high, Keller

and others (1998) conclude that "there is low potential for adverse ecological effects from levels of MTBE currently in surface waters, which are in the 10 to 100 µg/L level." Lake Tahoe water samples taken to determine the potential impact of boat activity on laboratory bioassay species indicated no observed detrimental effects.

In addition, *Health & Environmental Assessment of MTBE* by Keller and others (1998) describes

- health effects of MTBE by-products
- health considerations for ethanol
- research recommendations
- documentation for the extent of contamination of drinking water supplies

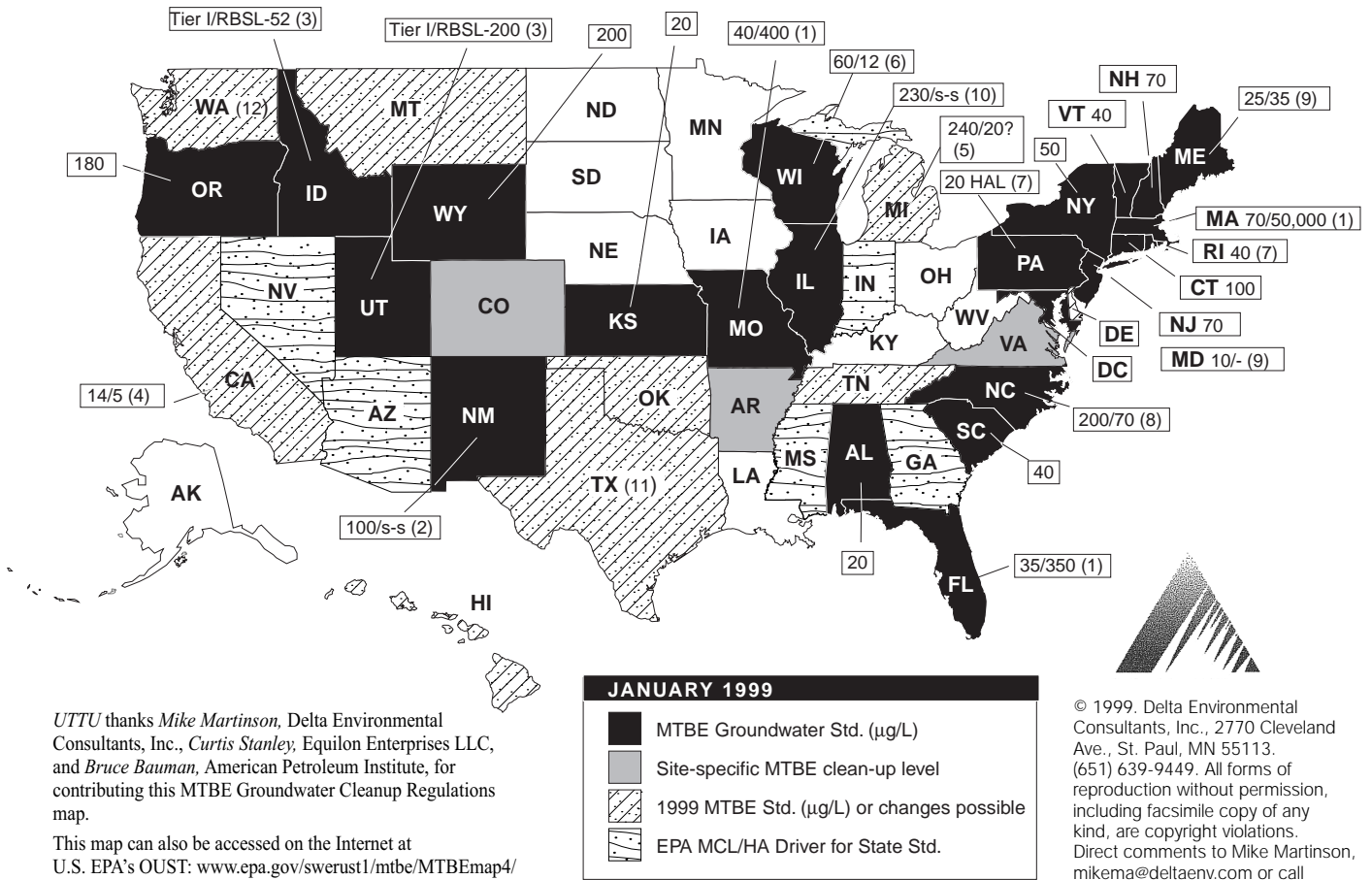
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Gestring, S. and D.C. Anderson, "MTBE Biodegradation and TBA," ASTSWMO MTBE Workgroup, newsletter #3, 1998; <http://www.astswmo.org/Publications/summaries.htm#MTBE>; also see the January 1999 newsletter.

Keller, A., Froines, J., Koshland, C., Reuter, J., Suffet, I. and J. Last, *Health & Environmental Assessment of MTBE: Report of the Governor and Legislature of the State of California as Sponsored by SB 521: Vol. 1, Summary & Recommendations*, Nov. 1998; <http://www.tsrtpt.ucdavis.edu/mtberpt/vol1.pdf>.

OFA, Oxygenated Fuels Association, 1998, <http://www.ofa.net>; the complete published report will be available soon on the IARC website, <http://www.iarc.fr>.

MTBE Groundwater Clean-up Regulations: Current and Future



UTTU thanks Mike Martinson, Delta Environmental Consultants, Inc., Curtis Stanley, Equilon Enterprises LLC, and Bruce Bauman, American Petroleum Institute, for contributing this MTBE Groundwater Cleanup Regulations map.

This map can also be accessed on the Internet at U.S. EPA's OUST: www.epa.gov/swrust1/mtbe/MTBEmap4/sld0001.htm.

Footnotes for MTBE map

- (1) Clean-up goal dependent on GW potable/non-potable use (e.g., 35/350)
- (2) Clean-up goal stated, but can also be site-specific (e.g., 100/s-s)
- (3) RBCA program Tier I/RBSL clean-up goal
- (4) Proposed Public Health Goal (PHG)/enforceable secondary standard
- (5) Considering draft MTBE standard (aesthetic) at 20 µg/L for 1999
- (6) WDNR NR 140 Enforcement Standard/Preventative Action Limit goals
- (7) HAL refers to health advisory limit
- (8) Remedial action goal/value used primarily for toxicology purposes
- (9) Action level/drinking water standard (i.e., MA 25/35 or MD 10/-)
- (10) IIEPA provisional enforcement level/site-specific clean-up goal possible
- (11) Evaluating Tier I MTBE values, currently not specified, for Revised Risk Reduction (RBCA) rule in 1999
- (12) Method A MTBE clean-up level (groundwater: 20 µg/L and soil: 0.1 mg/Kg) proposed in rule amendments for implementation in 1999



MTBE biodegradation studies

MTBE is widely regarded as being recalcitrant, or at the most, biodegradable under specific conditions. The conditions under which MTBE degrades are currently a subject of debate and research.

MTBE microcosm studies

These microcosm studies (Odenkrantz, 1998a) and their results were undertaken to identify MTBE's biodegradation potential:

- **1984 aerobic study:** MTBE recalcitrant (Fujiwara, T.T., Kinoshite, T., Sata, H. and L. Kojima, "Biodegradation and Bioconcentration of Alkylethers," *Yukagaku*, Vol. 33).
- **1985 aerobic study:** MTBE recalcitrant (Novak, J.T., Goldsmith, C.D., Benoit, R.E. and J.H. O'Brien, "Biodegradation of Methanol and Tertiary Butyl Alcohol in Sub-surface Systems," *Water Science and Technology*, Vol. 17)
- **1990 aerobic study:** MTBE recalcitrant (Jenson, H.M. and E. Arvin, "Solubility and Degradability of the Gasoline Additive MTBE and Gasoline Components in Water," in *Contaminated Soil*, editors A. Hinsenveld and W.J. van den Brink: Netherlands, Kluwer Academic Publishers).
- **1990 aerobic study:** MTBE recalcitrant (Barker, J.F., Hubbard, C.E. and L.A. Lemon, "The Influence of Methanol and MTBE on the Fate and Persistence of Monoaromatic Hydrocarbons in Groundwater," *Proceedings of the Conference on Petroleum Hydrocarbons and Organic Chemicals in Groundwater*, National Ground Water Association)
- **1993 anaerobic study:** MTBE no degradation (Sulfita, J.M. and M.R. Mormile, "Anaerobic Biodegradation of Known and Potential Gasoline Oxygenates in the Terrestrial Subsurface," *Environmental Science and Technology*, Vol. 27, No. 5)
- **1994 anaerobic, nitrifying study:** isolated strain (Salanitro, J.P., Diaz, L.A., Williams, M.P. and D.M. Imboden, "Isolation of a Bacterial Culture that Degraded Methyl t-Butyl Ether," *Applied and Environmental Microbiology*, Vol. 60, No. 7)
- **1994 anaerobic, denitrifying study:** MTBE limited degradation (Mormile M.R., Liu, S. and J.M. Sulfita, "Anaerobic Biodegradation of Gasoline Oxygenates: Extrapolation of Information to Multiple Sites and Redox Conditions," *Environmental Science and Technology*, Vol. 28, No. 9)
- **1994 anaerobic, denitrifying study:** MTBE recalcitrant (Yeh, C.K. and J.T. Novak, "Anaerobic Biodegradation of Gasoline Oxygenates in Soil," *Water Environment Research*, Vol. 66, No. 5)
- **1995 aerobic study:** MTBE slight loss of O₂, increase of CO₂ (Horan, C.M. and E.J. Brown, "Biodegradation and Inhibitory Effects of MTBE Added to Microbial Consortia," *Proceedings of the 10th Annual Conference on Hazardous Waste Research*, May 23-25, Manhattan, Kansas, Great Plains/Rocky Mountain Hazardous Substance Center)
- **1997 aerobic study:** MTBE 50 percent reduction to 1 to 2 mg/L (Borden, R.C., Daniel, R.A., LeBrun, L.E. and C.W. Davis, "Intrinsic Biodegradation of MTBE and BTEX in a Gasoline-Contaminated Aquifer," *Water Resources Research*, Vol. 33, No. 5)
- **1997 aerobic study:** MTBE 50 percent reduction to 1 to 2 mg/L (Schirmer M., Barker, J.F. and B.J. Butler, Natural Attenuation of MTBE at the Borden Field Site, presented at the 1997 Battelle International In-Situ Bioreclamation Symposium, New Orleans, Louisiana)
- **1997 aerobic study:** MTBE no degradation (Bovard, D.S. and K.H. Baker, "Effects of TCE and MTBE on Biodegradation of BTEX and BTEX Components," American Society of Microbiology Meeting and in preparation for the *Canadian Journal of Microbiology*)
- **1998 methanogenic study:** MTBE extensive degradation (U.S. EPA, "Research Strategy for Oxygenates in Water," publication from the Office of Research and Development)
- **1998: propane substrate study:** MTBE some degradation (Envirogen, R.C. Borden)
- **1998 aerobic/fixed film study:** MTBE some removal (R.C. Borden, Envirogen, personal communication, Newport Beach, California, March 10)

Studies reported by Gestring and Anderson (1998) include:

- **1995 fuel site study:** MTBE degraded at a rate of 0.18 percent/day near the source area; laboratory studies documented some MTBE degradation in aerobic microorganisms prepared from soil collected at the spill source; TBA was produced (Daniel in IOFAC, 1996, "Fuel Oxygenates and Water Quality: Current Understanding of Sources, Occurrence in Natural Waters, Environmental Behavior, Fate and Significance," Washington D.C. Office of Science and Technology Policy)
- **1997 study:** MTBE degraded into tert-butyl alcohol (TBA) and formaldehyde through microbial oxidation and hydrolysis; further oxidation resulted in the formation of formic acid; an additional microbial oxidation pathway indicates that MTBE may degrade to tert-butyl formate and water, then to TBA and formic acid (Steffan and others, "Biodegradation of the Gasoline-Oxygenated Methyl Tert-Butyl Ether and Tert-Amyl Methyl Ether Propane-Oxidizing Bacteria," *Applied and Environmental Microbiology*, Vol. 63, No. 11)

(See also studies in this issue's article, "MTBE study at the U.S.G.S. site in South Carolina".)

Odenrantz (1998a), describing another study where MTBE appeared to have traveled great distances, offers the following observations: "There is some evidence to support limited aerobic and anaerobic biodegradation of MTBE via microcosm studies conducted under both aerobic and anaerobic conditions. . . MTBE emanating from underground gasoline storage tanks can easily travel over 1,000 feet downgradient from its source, and there are reports of MTBE traveling as far as three miles from a source in groundwater. In the studies examined in some detail in this paper, there is no definite evidence that MTBE biodegrades intrinsically" . . .

In summary, Odenrantz found that MTBE

- is setting travel distance records in groundwater across the country
- seems resistant to biodegradation
- appears to persist in the subsurface environment

"Once MTBE enters an aquifer, its primary means of travel is through the path of least resistance (with the flow), and there is evidence to suggest its vertical migration is enhanced by infiltration (Odenrantz, 1998a).

Odenrantz (1998b) comments on the MTBE mass loss in the Borden Aquifer study, which some researchers have interpreted as "MTBE biodegraded". "The researchers found only 3 percent of the mass 8 years after the MTBE was injected. An analogy is trying to find all the smoke from a puff released to the outdoor air—7 hours after its release. Assume dispersion in air is 10,000 times that in water; 8 years is 70,080 hours. Any researcher who could find 3 percent of the mass from a puff of smoke 7 hours after it was released into the atmosphere would be a candidate for an award-winning paper." (Reviewer's note: *this analogy may be less meaningful if one considers that air flow is turbulent whereas groundwater flow is laminar.*) Odenrantz suggests that the mass of MTBE injected into the Borden Aquifer was lost by natural attenuation processes, which could include dispersion, dilution, adsorption, volatilization, biodegradation, and chemical or biological stabilization or destruction. In addition, it is very possible that the plume moved vertically through the aquitard below the aquifer.

"The work was excellent with respect to quantifying the natural attenuation of a small instantaneous amount of MTBE; however, there was absolutely no proof that biodegradation of MTBE occurred at all in groundwater" (Odenrantz, 1998b).

References

Gestring, S. and D. C. Anderson, "MTBE Biodegradation and TBA," ASTSWMO MTBE Workgroup, Newsletter #3, June 2, 1998; <http://www.astswmo.org/Publications/summaries.htm#MTBE>; Scott Gestring can be reached at 406-444-1388 and Dean C. Anderson at 609-777-1949.

Odenrantz, J.E., "Implications of MTBE for Intrinsic Remediation of Underground Fuel Tank Sites," 1998a, in *Proceedings of the 1998 Conference and Exposition on Petroleum Hydrocarbons and Organic Chemicals in Ground*

Water: Prevention, Detection and Remediation, November 11-13, 1998, Houston, Texas; National Ground Water Assoc., 614-898-7791, ngwa@ngwa.org; <http://www.ngwa.org>.

Odenrantz, J.E., "Toxic Soil and Water Forum," 1998b, *Remediation*, Autumn 1998.

UTTU thanks Joseph Odenrantz, founder and principal at Tri-S Environmental, Inc., Newport Beach, California 92660, 949-644-8602, for his help on this article and others in this issue.



Summary of MTBE remediation technologies

Creek and Davidson (1998) recently examined 14 MTBE remediation case studies to determine performance and cost of MTBE remedial techniques. Researchers considered hundreds of potential MTBE study sites before selecting the 14 sites for their study. The sites consisted of 11 service stations, 1 small UST site and 2 bulk plants. Sites were located in the following states:

- California (3 sites)
- Massachusetts (3 sites)
- New Jersey (3 sites)
- Florida (2 sites)
- Vermont (1 site)
- Wisconsin (1 site)
- one confidential site

Complete information on the sites is available from Davidson and others (1999; *publication pending*). Sites were analyzed for remedial design, and operational data were reviewed. These data consisted of

- pilot test results
- system flow rates
- remediation and treatment technology selections
- number of extraction/injection points
- system operation periods
- contaminant concentration in groundwater over time

To treat groundwater, remediators used air stripping, liquid-phase carbon adsorption and advanced oxidation. The actual remedial systems consisted of

- groundwater extraction systems (pump and treat), 6 sites
- groundwater extraction systems combined with soil vapor extraction, 5 sites
- soil vapor extraction (SVE) system, 1 site
- soil vapor extraction system combined with air sparging, 1 site
- biosparge system, 1 site

Groundwater extraction

Six sites used groundwater extraction solely while five sites used groundwater extraction with soil vapor extraction (SVE) and/or air sparging. Groundwater was extracted at rates ranging from 0.5 to 800 gallons per minute (gpm). Because MTBE is highly soluble and is minimally retarded, remediators expected this technology to work well, and it did. At all seven sites for which full data were available, the MTBE concentration in the influent water declined 1.4 to 7 times more than did the benzene over the entire time range. Data indicated that preferential removal of dissolved-phase MTBE occurred at most sites, despite variances of starting concentrations, geology and pumping rates.

Air stripping

Because MTBE has a lower Henry's law constant than BTEX compounds, air stripping of MTBE will not be as efficient as for BTEX. In this study, air stripping was the most commonly applied technology for removing dissolved MTBE from water. Researchers found the following:

- removal rates varied from 92 to 99 percent
- the technology was robust, indicated by success over a wide range of water flow rates (0.5 to 800 gpm) and a wide range of initial influent MTBE concentrations (96 µg/L to 56,000 µg/L)
- the technology was reliable, i.e., downtime was minimal
- one site switched from air stripping to carbon adsorption because treating the stripper off-gas became difficult and expensive
- another site experienced biofouling in the packing; MTBE removal rate plummeted from 92 percent to 26 percent following the biofouling incident
- the technique indicated that MTBE removal efficiencies can be 95 percent or more when the air:water ratios are greater than 175:1

Liquid-phase carbon adsorption

Eight sites used adsorption to granulated activated carbon (GAC) for water treatment. MTBE has a low affinity to most activated carbons, and for all of the sites except one, this treatment was not successful. Rapid GAC utilization and MTBE break-through led remediators to discontinue the treatment. Researchers found

- GAC can adsorb MTBE to some degree
- MTBE readily desorbs from the GAC vessels and often breaks through quickly compared to BTEX
- coconut shell carbon is expected to be more effective for MTBE removal than coal-based carbon; using high-quality virgin carbon is important for good treatment performance

- natural organic matter and other compounds (e.g., BTEX, TPH) reduce MTBE's removal efficiency
- pilot tests are helpful
- to improve efficiency, GAC vessels will likely be required in series
- remediators should consider taking more frequent water analyses to detect the sudden breakthrough of MTBE

Advanced oxidation

The best advanced oxidation treatment for MTBE has not yet been identified. In this study, one multi-component oxidation system used UV light, hydrogen peroxide and ozone with a molybdenum catalyst. This pilot scale oxidation system achieved good MTBE destruction, greater than 80 percent. The full-scale operation, however, created residual hydrogen peroxide and residual ozone in the effluent water that resulted in corrosion and mechanical failure. As a result, the system required extensive downtime as well as high labor and capital costs. Other results:

- oxidation is a good technology for MTBE, but its application must be handled carefully
- pilot testing in the field is recommended
- consideration should be given to use of advanced oxidation as part of a treatment train
- creation of daughter products and by-products are a concern

Air sparging/biosparging

Air sparging success was mixed. Two sites in this study used air sparging. During sparging at one site, MTBE vapors increased in the vadose zone while MTBE levels decreased in groundwater. Remediators also noted increased dissolved oxygen levels, indicating that oxygen was added to the groundwater. They did not address if the dissolved oxygen impacted MTBE levels by enhancing biodegradation, although it was clear the system certainly caused MTBE volatilization. The results, however, were mixed because long-term sampling of the site—2.5 years—revealed that some control wells showed the same MTBE decline as wells in the treated areas.

At another site, biosparging appeared to accelerate the natural degradation and attenuation, but MTBE was following a declining trend before the sparging was initiated. Again, attributing MTBE reductions to biosparging was not definitive.

Soil vapor extraction

Researchers expected that soil vapor extraction would be more applicable to MTBE removal than to BTEX because of MTBE's high vapor pressure. (*Reviewer's note: MTBE's Henry's law constant, however, makes MTBE difficult to get out of water and, by analogy, soil too.*) Sites undergoing SVE and pump-and-treat had greater MTBE concentration decreases than sites undergoing only pump-and-treat. Most of the sites did not sample extracted vapors specifically for MTBE, so system performance could not be ascertained. At one site where the extracted vapors were measured, MTBE made up 41 percent of the combined MTBE and TPH extracted, although 5 months later, MTBE extraction declined to 26 percent. The percentage of MTBE in the extracted vapors decreased as SVE continued.

One site that used only SVE for remediation (data available for 2.2 years) showed a decrease in MTBE levels indicated by dissolved-phase MTBE in groundwater. Results from one well showed a 16-fold decrease in MTBE. Other wells showed decreases up to 1,340-fold. "It is possible that the SVE operations here prevented contaminant recharge to the groundwater system, thus resulting in these dissolved-phase concentration declines. This, however, requires confirmation and a better understanding of MTBE storage and movement in the vadose zone" (*Creek and Davidson, 1998*).

MTBE remediation cost

Of the 14 systems studied, 10 are still operating, thus final costs are not available. *Creek and Davidson (1998)* give in their paper a breakdown of capital and annual operation and maintenance costs, but they caution readers that the costs vary in accuracy and should be used only as order of magnitude estimates. In general, treatment costs ranged from \$44,000/yr for a partial pump-and-treat system to \$575,000 for a large treatment system. Annual operation ranged from \$18,000 for a small SVE system to \$120,000 for a large-scale pump-and-treat.

Creek and Davidson (1998) concluded that "Subsurface MTBE contamination can be remediated with currently available technologies, though there will typically be an increase in costs in comparison to treating water with other contaminants characteristic of gasoline spills. The precise impacts of MTBE on remediation costs have not been well established."

Anecdotal estimates of the increased costs of remediating a hydrocarbon-contaminated site with MTBE range from 10 to 500 percent.

"Because of MTBE's reduced volatility, reduced biodegradation and possibly larger plume sizes, the presence of MTBE can impact the remedial technology selections, the project scope and efficiency of the removal and treatment systems. Therefore, depending upon the site specifics, the presence of MTBE can cause minor to severe cost impacts to hydrocarbon remediation projects. The greatest cost increases will likely occur at sites where monitored natural attenuation would have been acceptable for the BTEX/TPH plume, but the

mobile MTBE plume mandates operating an active remediation and treatment system. To minimize plume expansion and thus avoid significant remedial costs increases, it is recommended that when MTBE remediation is required, the remediation plans should be implemented expeditiously" (*Creek and Davidson, 1998*).

Conclusions

The authors concluded the following:

- groundwater extraction is effective for removing dissolved-phase MTBE; concentration trends of extracted water and groundwater in monitoring wells indicate preferential MTBE removal vs. benzene
- air stripping is effective for MTBE removal at air:water ratios above approximately 180:1 (i.e. 2 to 4 times greater than the air flow required for BTEX removal); this technology was effective for a wide range of influent concentrations and a wide range of flow rates
- activated carbon performed poorly for removing dissolved-phase MTBE from water, resulting in rapid breakthrough and frequent carbon change-out requirements; however, use of GAC as a polishing step or for low MTBE levels may be cost-effective, particularly if virgin, coconut shell carbon is used
- advanced oxidation is promising; however, currently available methods need to be refined if advanced oxidation is to be cost effective
- soil vapor extraction is promising for MTBE removal from the vadose zone; limited field data indicate preferential removal in comparison to BTEX compounds
- an air sparging performance test indicated measurable and significant MTBE volatilization from groundwater; however, time-series field data are inconclusive regarding air sparging or biosparging's effectiveness
- many factors—spill history, geology, technology used—influence cost of remediating MTBE, and the costs provided in this paper should only be used for order-of-magnitude comparison

Kansas data

The Kansas Department of Health and Environment (KDHE) Storage Tank Section has been studying MTBE since 1991. Consequently, KDHE has found MTBE at more than 900 sites, 60 of which are being actively remediated (*Hattan and Blackburn, 1999*).

"An evaluation of 60 MTBE remedial sites reveals that most of the traditional technologies are somewhat effective in reducing MTBE concentrations." These technologies include soil vapor extraction (SVE), air sparging (AS), pump-and-treat and use of Oxygen Release Compound (ORC). At 43 percent of the sites, MTBE went to non-detect, while 23 percent of the sites had a 90 percent MTBE reduction.

"MTBE concentration reductions ranging between 50 percent and 90 percent were observed at 12 percent of the sites, while 10 percent showed less than 50 percent reduction." At 12 percent of the sites, MTBE actually increased (Hattan and Blackburn, 1999).

Eighty percent of the sites using a combination AS/SVE technology showed an MTBE reduction greater than 90 percent; these statistics, however, are based on a limited evaluation of the technologies, such as duration of the remediation. This is compared to a 27 percent reduction in MTBE concentrations at monitored-only sites.

Additional information

Additional information on MTBE remediation technologies can be found at the Association of California Water Agencies website, <http://www.acwanet.com/research/index1.html>. Of interest is the report *Treatment Technologies for Removal of MTBE for Drinking Water*, published in December 1998. The report can be ordered by calling 916-441-4545.

References

Hattan, G. and G. Blackburn, Association of State and Territorial Solid Waste Management Officials, January 1999, *ASTSWMO MTBE Workgroup Newsletter*, Vol. 2, No.1, "Findings of Kansas MTBE Investigations"; <http://www.astswmo.org/Publications/summaries.htm#MTBE>.

Creek, D.N. and J.M. Davidson, "The Performance and Cost of MTBE Remediation Technologies," *Proceedings of the 1998 Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Remediation*, sponsored by NGWA, 800-551-7379; e-mail: ngwa@ngwa.org; <http://www.ngwa.org>.

Davidson, J.M., Creek, D.N. and R. Parsons, "MTBE Remediation: An Evaluation of Technologies, Field Experiences and Case Studies," 1999, publication pending.

See also, Davidson, J.M. and D.N. Creek, 1999, "Using the Gasoline Additive MTBE in Forensic Environmental Investigations," *International Journal of Environmental Forensics*, available at <http://www.aehs.com/ijethomepage.html>.

UTTU thanks Jim Davidson, Alpine Environmental, Inc., Fort Collins, Colorado, for his help on this article.



Selected annotated references on MTBE

Following are selected references on MTBE. Note that the Brachtl and others (1997) citation contains a list of 268 references.

Association of State and Territorial Solid Waste Management Officials (ASTSWMO) MTBE Workgroup Newsletters, phone 202-624-5828; <http://www.astswmo.org/Publications/summaries.htm#MTBE>. The newsletters "study the magnitude of the MTBE problem and discuss the experiences and concerns of regulatory agencies and industry . . . the goal of the workgroup is to function as a clearinghouse for new information and to communicate MTBE issues to states through a quarterly newsletter." The newsletters contain sections on recent MTBE developments, MTBE surveys, health advisories, MTBE news from states, research, remediation, legislation, conferences and other sources of information. To contribute to the MTBE Workgroup, contact Jeff Kuhn at 406-444-5976 (jkuhn@mt.gov) or Pat Ellis at 302-395-2500 (pellis@DNREC.STATE.DE.US). These newsletters are an excellent source of information on MTBE.

Brachtl, E.V., Price, C.V. and R.M. Clawges, "Selected Bibliography of the Fuel Oxygenate Methyl tert-Butyl Ether (MTBE) with Emphasis on Water Quality," 1997, U.S. Geological Survey, Open-File Report 97-564; for additional information write the District Chief, U.S. Geological Survey, 1608 Mt. View Road, Rapid City, South Dakota 57702. The bibliography contains 268 MTBE references listed alphabetically by author. A keyword index, which appears at the document's end, is correlated by a number (1 to 268) to the pertinent documents. See U.S. Geological Survey websites below.

Disperse is an advection/dispersion model for MTBE and TBA, written by Paul Bauer (PBauer@dep.state.nj.us) of the New Jersey Department of Environmental Protection. The easy-to-use model calculates conservative estimates for the size and duration of MTBE and TBA plumes, using an accepted advection/dispersion equation. It is not intended to be a highly accurate predictor of actual site data; instead, the model represents the potential worst case scenario. Actual plume size and duration will be less in most cases. The conditions and assumptions of the model, and the model itself can be found at <http://www.state.nj.us/dep/srp/regs/guidance.htm#disperse>.

Rathburn, R.E., "Transport, Behavior and Fate of Volatile Organic Compounds in Streams," U.S. Geological Survey Professional Paper 1589, 1998; to obtain, write U.S. Geological Services, Box 25286, Federal Center, Denver, Colorado 80225.

R-UNSAT is a computer model that quantifies volatilization and biodegradation rates for organic compounds near the water table. It can also be applied to other unsaturated zone transport problems involving gas diffusion and deposition of compounds from the atmosphere to shallow groundwater. R-UNSAT simulates reactive, multispecies transport in a layered unsaturated zone with variable moisture content. Biogeochemical reactions can be sources or sinks for each species, modeled using zero-order or first-order kinetics. R-UNSAT is being used to quantify rates of mass transfer of MTBE and BTEX from groundwater to the unsaturated zone. Documentation, code and executable version can be found at <http://www.nj.er.usgs.gov/>; additional information on the U.S. Geological Survey's Toxic Substances Hydrology Program can be found at <http://toxics.usgs.gov/toxics>.

Web sites

American Petroleum Institute MTBE Database, <http://www.api.org/news/896mtbe2.htm>; and <http://www.api.org/ehs/mtbelink.htm>, which contains laboratory research on the cometabolism of gasoline oxygenates by alkane-utilizing bacteria

California EPA Briefing Paper <http://www.crl.com/~pi/project/smog/MTBE.html>

California Issue Paper on MTBE <http://www.calepa.cahwet.gov/epadocs/mtbe.txt>

California Legislation <http://www.acwanet.com/legislation/legis/mtbe2.html>, and <http://www.acwanet.com/news/whatsnew/MTBEnr.html>

Dupont-Dow Research on oxygenates, <http://www.dupont.com/products/viton/lkprev.html>

National Science and Technology Council, Interagency Assessment of Oxygenated Fuels Report <http://www.gcric.org>

Maine DEP MTBE Questions and Answers <http://www.state.me.us/dep/rwm/mtbeqa.htm>

Nation-Wide Account of MTBE problem <http://www.newsday.com/news/tanks/ncovmon.htm>

OSTP Report on Oxygenates/MTBE <http://www.epa.gov.OMSWWW/whatsn97.htm>

OUST MTBE, <http://www.epa.gov/OUST/mtbe>

Oxygenated Fuels Association (OFA) <http://www.ofa.net>, which contains the report "Taste and Odor Properties of Methyl Tertiary-Butyl Ether and Implications for Setting a Secondary Maximum Contaminant Level"

U.S. EPA Office of Water, Standards and Advisories <http://www.epa.gov/docs/ostwater/tools/dwstds-s.html>

U.S. EPA Provisional Health Advisory <http://www.epa.gov/OST/Tools/MtBEaa.pdf>

U.S. EPA Research Strategy on Oxygenates <http://www.epa.gov.ncea.oxywater.htm>

U.S. Geological Survey, MTBE Bibliography (sorted by date of entry, keywords, free text or author) <http://www.sd.cr.usgs.gov/nawqa/vocns/mtbe/bib/>, more than 319 references

U.S. Geological Survey (containing many links to California websites, API, EPA, and reports, projects and raw data) <http://water.we.usgs.gov/mtbe/>

UTTU obtained many of these sites from ASTSWMO newsletter (see above).

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Late note: U.S. EPA directive

Use of monitored natural attenuation (MNA) at Superfund, RCRA, corrective action and underground storage tank sites

EPA's Office of Solid Waste and Emergency Response recently published its directive on monitored natural attenuation (MNA). Sections contained in the document include

- overview
- contaminants of concern
- transformation products
- cross-media transfer
- petroleum-related contaminants
- chlorinated solvents
- inorganics
- advantages and disadvantages of MNA
- implementation
- role of MNA in OSWER remediation programs
- demonstrating the efficacy of natural attenuation through site characterization
- sites where natural attenuation may be appropriate
- reasonable timeframe for remediation
- remediation of sources
- performance monitoring and evaluation
- contingency remedies

The EPA does not view MNA as a "no action" remedy but rather as a means of addressing contamination under a limited set of site circumstances. The EPA is confident that, at many sites, MNA will be a reasonable and protective component of a broader remediation strategy. The EPA believes, however, that at many other sites either the uncertainties will be too great or the need for a more rapid remediation will preclude the use of MNA as a stand-alone remedy. This directive should help promote consistency in how MNA remedies are proposed, evaluated and approved.

Directive 9200.4-17P can be obtained from state UST/LUST managers. It can also be found by searching OUST's web site, <http://www.epa.gov/OUST/>.

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