MTBE in Groundwater: Status and Remediation

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Introduction

The addition of methyl *tertiary*-butyl ether (MTBE) to gasoline became controversial after its detection in waters of the United States. Probably the beginning of widespread public concern about MTBE came about after the detection of MTBE in the drinking water of the City of Santa Monica, Calif. Fifty percent of Santa Monica's drinking water came from groundwater, which was found to be contaminated by underground storage tanks (UST). In August 1995, MTBE was detected in groundwater from one of two well fields, and by April 1996, the concentration was up to 610 μg/L. All of the wells from that well field (the Charnock) were closed (USEPA 2000). Additionally, the United States Geological Survey (USGS) National Water Quality Assessment Program (NAWQA) found that MTBE was detected at a frequency of 16.9% in wells in urban areas and 3.4% in wells in rural areas (Squillace et al. 1999) (Fig. 1). Of 60 volatile organic compounds (VOC), only trichloromethane (chloroform) was detected with greater frequency. This result is rather remarkable, as MTBE has only recently been widely used as a gasoline additive.

A more recent joint USGS/EPA study of 12 northeastern states that is examining MTBE and other VOC data in a random sampling of 20% of their drinking water supplies has so far detected MTBE in 7% of drinking water samples, with only 0.8% of the detected amount over 20 μg/L (the lower boundary of EPA's consumer advisory) (USEPA 2000). The joint USGS/EPA study also found that MTBE was detected more frequently in drinking water from areas with RFG or Oxyfuel than in areas without these fuel types and that there was very little cooccurrence of BTEX (benzene, toluene, ethylbenzene, and xylenes) with the detection of MTBE.

MTBE was initially added to gasoline to boost performance in the 1970s as alkyl lead additives were discontinued and was later added to improve air quality in accordance with the Clean Air Act (CAA) Amendments of 1990. In 1992, oxygenated gasoline was required in areas that did not meet the carbon monoxide standard during the winter (Wintertime Oxyfuel program). In 1995, nine ozone nonattainment areas were required to use reformulated gasoline (RFG) containing oxygenates year round. MTBE is added at concentrations from 11 to 15% by volume to oxyfuels and RFG (Fig. 2). It is the most commonly used oxygenate in RFG because it is low cost and produced from compounds available at most refineries (methanol, from natural gas and isobutylene, a refinery by-product) (Squillace et al. 1997). It also blends easily with gasoline and can be shipped through existing pipelines.

MTBE in drinking water causes taste and odor problems. It has a distinctive and unpleasant turpentine-like taste and odor that can be detected at concentrations as low as 2.5 ppb for odor and 2.0 ppb for taste (USEPA 2000). The California Department of Health and Safety has proposed a secondary maximum contaminant level of 5 ppb for MTBE based on taste and odor concerns (Keller et al. 1998).

MTBE is classified as a possible human carcinogen by the EPA as a result of inhalation cancer tests (USEPA 2000). In 1997, the EPA concluded that there was not enough information available on MTBE health effects and exposure to establish a national primary drinking water regulation, and there was a low probability that MTBE between 20 and 40 μg/L would cause adverse health effects. Some states have established their own standards. For example, California and New Hampshire have proposed drinking water standards of 13 μg/L (USEPA 2000).

MTBE has also been detected in lakes and reservoirs (Fig. 1) coming mostly from watercraft emissions, discharge of contaminated groundwater, fallout from precipitation, storm water runoff or direct releases (Squillace et al. 1997). Reuter et al. (1998) conducted a study at Donner Lake, Calif. and found that MTBE levels rose significantly from 0.1 μg/L during the winter season to 12.1 μg/L during the summer (boating season). The Metropolitan Water District of Southern California (Dale et al. 1998) conducted an MTBE monitoring program in six surface water reservoirs and observed that the occurrence of MTBE was correlated to the pattern of recreational use by motorized watercraft. In Shasta Lake, a recreational-use reservoir in California, MTBE concentrations over the 1996 Labor Day weekend ranged between 9 and 88 μg/L. The maximum values were associated with large boats entering the docking area or with engine exhaust from the boats (USEPA 2000).

Elevated levels of MTBE in the Merrimack River, Massachusetts were detected after a release of approximately 11,000 gallons of gasoline from a tanker truck. The cities of Tewksbury, Methuen, and Lawrence, which use the river as their drinking water supply, had to temporally close their water treatment plants until MTBE concentrations dropped to safe levels (USEPA 2000).

A study of MTBE in California's drinking water (California Department of Health Services 2002) shows that out of 670 surface water sources sampled, 31 sources (4.6%) exhibited measurable levels of MTBE, with 10 sources having levels higher than 5 μg/L.

As a result of the growing concern about MTBE, the U.S. Environmental Protection Agency convened a panel, known as the Blue Ribbon Panel, in November 1998 to investigate water and air quality issues associated with the use of oxygenates in gasoline. The Blue Ribbon Panel recommended improvements to the nation's water protection programs, reduction in the use of MTBE, removal by Congress of the Clean Air Act requirement

Fig. 1. MTBE detections in ambient ground water (NAWQA Program) and in source waters (National MTBE Survey) (from Clawges et al. 2000)

that 2% by weight of RFG consist of oxygen, and that EPA act to retain air quality improvements brought about by using MTBE (USEPA 1999).

Some states have taken more agressive action. The governor of California issued an executive order in March 1999 to the Air Resources Board to develop a timetable for the removal of MTBE from gasoline by no later than December 31, 2002. Maine opted out of the reformulated gasoline program in March 1999. New Hampshire enacted a law in July 1999 aimed at reducing the use of MTBE. The law also required that the state request a waiver from the EPA about meeting RFG requirements until 2002. Arizona, Kansas, Missouri, New York, and South Dakota have either proposed bans, phase-outs, or limited the use of MTBE (USEPA 2000).

MTBE's physical and chemical properties have given the environmental industry cause for concern. It has a relatively high water solubility (approximately 50,000 mg/L) (Table 1), so it can achieve higher dissolved concentrations in groundwater than other gasoline components. It has a lower affinity for sorption than other gasoline components as can be seen in Table 1 and therefore moves with a velocity close to that of groundwater. Its low Henry's law constant leads to its partitioning to the water phase rather than air.

As a result, MTBE's fate and transport in the environment has been an area of active research in recent years. The biodegradation of MTBE in laboratory and field settings has been the subject of numerous studies. As with most subjects of active research, the prevailing wisdom about MTBE's biodegradability has shifted during the last decade or so. Early laboratory research (Suflita and Mormile 1993), and site investigations indicated that MTBE was recalcitrant. Further research showed that MTBE could be biodegraded (Salanitro et al. 1994). Some field studies have indicated that MTBE is degraded by adapted native microorganisms (Borden et al. 1997). Other field studies have shown that amendments of chemicals (oxygen, cosubstrates) and microorganisms (MTBE degraders) are necessary for MTBE biodegradation.

This article outlines the state of knowledge on plume behavior in groundwater. Our current understanding of aerobic and anaerobic biodegradation of MTBE in both field and laboratory studies is presented next followed by a detailed discussion of MTBE remediation using natural attenuation and bioremediation technologies among others. The article is not intended as an exhaustive analysis of MTBE remediation but rather as a retrospective of what progress has been accomplished to date.

Methyl *tertiary*-Butyl Ether in Groundwater—Plume Studies

Several large-scale studies of MTBE and BTEX plumes have compared the detection and concentration of BTEX and MTBE in groundwater and plume lengths to predict the impact of MTBE on groundwater resources using either state databases or corporate records. In a 1998 report at Lawrence Livermore (Happel et al. 1998), the impact of MTBE on groundwater in California was analyzed. They studied data from 236 leaking underground fuel tank (LUFT) sites and found that MTBE was detected at 78% of the sites in 1995–1996. Based on data from San Diego County, Happel et al. (1998) found that the detection of MTBE and BTEX together in one monitoring well decreased over a period of 3 years, from 80 to 60%. During this same time, MTBE and BTEX were detected with the same frequency. Because the authors as-

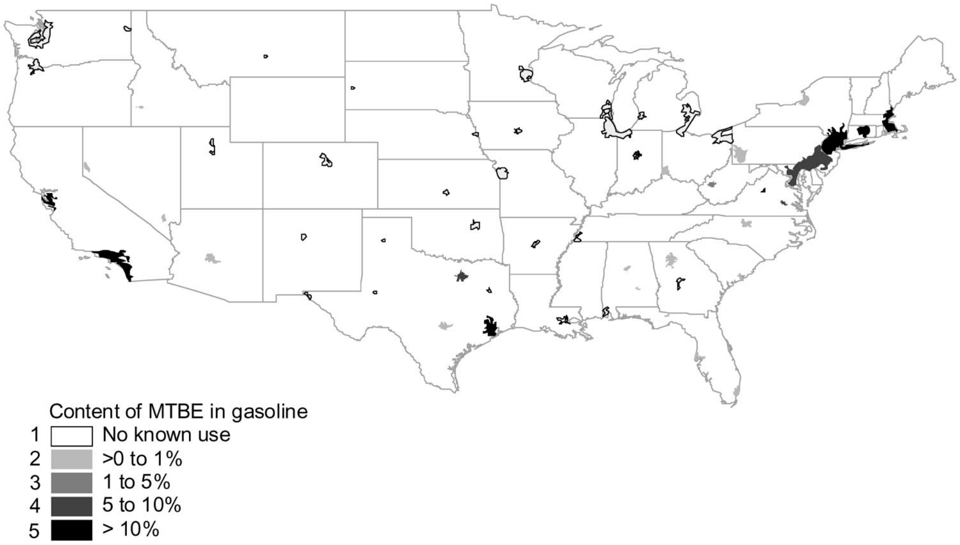

Fig. 2. Content of MTBE in gasoline, Winter 1997–98 (from Clawges et al. 2000)

sumed that the majority of BTEX plumes are stable (which is a good assumption), the dissociation of MTBE from BTEX suggested that the MTBE plumes are separating from the BTEX plumes and moving from BTEX-impacted to non-BTEX-impacted wells. In downgradient wells, the concentration of MTBE was equal to or higher than BTEX, implying that MTBE will be leaving the existing monitoring networks. The benzene concentration decreased by several orders of magnitude in downgradient wells, which is indicative of natural attenuation through biodegradation, but MTBE concentrations decreased by only one order of magnitude, which is more indicative of natural attenuation by dispersion. However, the data are limited, and the authors recognized the need to examine the MTBE plumes in the future when more monitoring results are available.

A similar study conducted in Texas by Mace and Choi (1998) used a database that had 609 sites with at least one detection of MTBE. MTBE was above the detection limit in groundwater at 93% of the 609 sites. Seventy-three percent of the sites had maximum concentrations above 200 μg/L, and 28% had maximum concentrations above 10,000 μg/L. At the 100 μg/L concentration, MTBE plumes had a median length of 50 m (163 ft) and a geometric mean length of 59 m (195 ft); whereas, benzene plumes were 43 m (141 ft) in median length, with a geometric mean length of 48 m (156 ft).

A few sites had enough data to allow examination of concentrations over time in specific wells or examination of the plumes over time. The authors did not observe an increase in MTBE concentration at any wells, possibly because the monitoring wells in the database are not at the leading edge of the MTBE plume. The authors stated that the MTBE concentrations seem stable or decreasing at many of the leaking petroleum storage tank (LPST) sites, which may be evidence of natural attenuation of MTBE.

Buscheck et al. (1998) reported on a plume study at service station sites across the United States. MTBE and benzene data were available for over 700 sites, and total petroleum hydrocarbon (TPH) data were available for most of these sites. The authors found that MTBE was detected at the highest percentage of sites in states where MTBE has been in use the longest (Texas 96%,

Table 1. Chemical Properties of Selected Hydrocarbon Compounds

Compound	Vapor pressure (mm Hg at 20°C)	Solubility (mg/L)	Henry's law constant (dimensionless)	log K_{oc} (at 20–25°C)
Aromatic gasoline hydrocarbons[a]				
Benzene	95.2	1,750	0.22	1.58
Toluene	30.0	515	0.26	2.13
Ethylbenzene	10.0	152	0.32	1.98
Xylenes (mixed isomers)	7.0	198	0.29	2.38
Chlorinated solvents[a]				
Tetrachloroethylene (PCE)	19.0	143	1.21	2.43
Trichloroethylene (TCE)	58.0	1,000	0.417	1.26
Oxygenates[b]				
Methyl tertiary butyl ether (MTBE)	240	48,000	0.022 to 0.12	0.55 to 0.91
Ethyl tertiary butyl ether (ETBE)	130	12,000	0.11	NA
Tertiary amyl methyl ether (TAME)	75	12,000	0.081	NA
Diisopropyl ether (DIPE)	159	2,000	0.199	1.13

Note: NA = not available.

[a] From Wiedemeier et al. (1999).

[b] From USEPA (1998).

Maryland 98%, California 83%). High concentrations of MTBE in groundwater also varied geographically, with concentrations exceeding 1 mg/L at 81% of Maryland service station sites and only 48% of California sites. California required tank upgrades before other states did, which may contribute to its lower MTBE detection rates and concentrations. At 69% of the sites in California, the benzene concentration was less than, 1,000 μg/L, and the sites could be closed (174 out of 251) if benzene was the only risk driver. Unfortunately, of these 174 sites, 123 had MTBE concentrations greater than 35 μg/L and were therefore unlikely to be closed easily. Overall observations from the time series data were that MTBE decreased only when benzene decreased, but MTBE could increase independently of benzene.

Another plume study was conducted by BP Amoco to investigate MTBE and benzene plume behavior (Reisinger et al. 2000). MTBE was detected in 38.9% of the samples, and benzene was detected in 42.8% of the samples. The mean MTBE concentration was 317 μg/L, and the mean benzene concentration was 365 μg/L. The mean length of MTBE plumes using the 10 μg/L contour was 43 m (140 ft); the mean length of benzene plumes using the 10 μg/L contour was 35 m (115 ft). MTBE plumes overall were 18% longer than benzene plumes and 52% larger than benzene plumes. Using well-specific time series data, the authors determined that 4.4% of the MTBE plumes were growing (2 out of 45), 6.6% were stable (3 of 45), and 89% were decreasing.

The above studies were mainly aimed at understanding plume behavior, but none of them addressed biodegradation of MTBE at the field scale.

Methyl *tertiary*-Butyl Ether Biodegradation

Initial studies on the biodegradation of MTBE reported negative results. Fujiwara et al. (1984) did not observe aerobic degradation of 100 mg/L MTBE by activated sludge. Jensen and Arvin (1990) found no aerobic degradation of 10 mg/L MTBE in activated sludge, aquifer material, or topsoil. Suflita and Mormile (1993) reported that MTBE did not degrade under methanogenic conditions. They determined that oxygenates with a tertiary or quaternary carbon atom were more recalcitrant than unbranched or slightly branched related chemicals. For example, butyl methyl ether was easily degraded but MTBE was not. Salanitro et al. (1994) attributed the recalcitrance of MTBE to the chemically unreactive and stable ether bond.

Over the last 8 years, aerobic MTBE degradation has been observed repeatedly in the laboratory, with mixed consortia, pure cultures, as a sole carbon and energy source, or cometabolically. However, MTBE biodegradation, when it does occur, is often slow, even under aerobic conditions (Salanitro et al. 1994). It has been speculated that MTBE may inhibit metabolism or electron transport or uncouple ATP formation (Salanitro et al. 1994). It is also possible that an intermediate along the degradation pathway is resistant to further degradation. However, some researchers are now finding organisms with relatively rapid aerobic growth on MTBE (Hanson et al. 1999; Steffan 2002). Successful anaerobic degradation of MTBE has also been reported, and this continues to be an active area of research.

Aerobic biodegradation of MTBE using mixed microbial cultures has been reported by a number of researchers. Aerobic MTBE biodegradation in the laboratory was first reported by Salanitro et al. (1994) using a mixed culture, BC-1, that was enriched from the biotreater sludge of a chemical plant. In later work, Salanitro et al. (1996) observed that the mixed culture BC-1 produced TBA, which was then metabolized via isopropanol and acetone. Cowan and Park (1996) examined oxygenate biodegradation and oxygen uptake with a MTBE-degrading enrichment culture from a petroleum refinery wastewater treatment plant. All five target oxygenate compounds—MTBE, ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), *tert*-butyl alcohol (TBA), and *tert*-amyl alcohol (TAA)—were degraded. In a later work, Park and Cowan (1997) used respirometry to determine the effects of temperature and dissolved oxygen (DO) on MTBE degradation by mixed cultures acclimated to MTBE. Miller et al. (1997) used two parallel GAC (granular activated carbon) bioreactors to treat groundwater contaminated with petroleum hydrocarbons and chlorinated solvents (TPH and BTEX removals were 80% and $>99\%$, respectively). MTBE removal was high for the first two weeks (99%), but then declined to 9%, probably as a result of sorption. After MTBE-degrading cultures were added, MTBE removal improved to $>75\%$.

Biodegradation of MTBE was observed in sediments from two gasoline-contaminated sites amended with uniformly labeled ^{14}C-MTBE and ^{14}C-TBA (Bradley et al. 1999). The authors then surveyed stream- and lake-bed sediments from 11 sites around the United States (Bradley et al. 2001b) and reported mineralization in all sediments at a range of 15–66% after 50 days of incubation. The authors attributed the persistence (especially seasonal) of MTBE in some surface water systems to be due to recontamination rather than recalcitrance. MTBE biodegradation by mixed cultures was also reported using laboratory-scale biotrickling (Fortin and Deshusses 1999), a biofilm from a MTBE-contaminated site and uniformly labeled ^{14}C-MTBE (Landmeyer et al. 2001), enrichment microcosms prepared from MTBE-degrading Borden aquifer material, and in uncontaminated Borden aquifer material (Hunkeler et al. 2001).

Several studies have also reported aerobic biodegradation of MTBE by pure cultures. Mo et al. (1995) and Mo et al. (1997) isolated several bacterial strains from sludge that could degrade MTBE as the sole carbon source. Hanson et al. (1999) observed MTBE biodegradation by the strain PM1 (isolated from a compost biofilter consortium that could degrade MTBE). Also, Salanitro et al. (2001) isolated the species in the MC-100 consortium responsible for MTBE degradation and identified it as *Rhodococcus* sp. nov. Other pure cultures have been used in MTBE biodegradation research (Hardison et al. 1997; Hatzinger et al. 2001; Steffan et al. 1997; Garnier et al. 1999; Hyman et al. 1998).

Aerobic biodegradation of MTBE-contaminant mixtures has also been the subject of a number of studies. When MTBE occurs as part of a mixture of contaminants, MTBE might inhibit the biodegradation of cocontaminants. Jensen and Arvin (1990) reported that 200 mg/L MTBE had a slight inhibitory effect on degradation of the aromatic hydrocarbons benzene, toluene, ethylbenzene, o/m xylene, and naphthalene, but 40 mg/L MTBE had no effect on degradation. MTBE at a concentration of 740 mg/L inhibited the mineralization potential of hexadecane by 50% (Horan and Brown 1995). Conversely, Fujiwara et al. (1984) found that 12.5% MTBE in gasoline did not affect gasoline degradation. Salanitro et al. (1996) determined that 5–90 mg/L MTBE did not affect the degradation rate of BTEX compounds present at 2–2.5 mg/L.

Another issue with mixtures of contaminants is whether MTBE biodegradation is affected by the presence of other contaminants. Mo et al. (1995) found that *t*-butanol, butylformate, isopropanol, acetone, and pyruvate reduced MTBE biodegradation in seven strains, but pregrowth on *t*-butanol followed by transfer to MTBE only increased MTBE degradation. In a later study, Mo et al. (1997) found that MTBE degradation decreased if the isolates were exposed to MTBE plus *t*-butanol, butyl formate, isopropanol, acetone, and pyruvate. Other studies that show inhibition of MTBE biodegradation due to BTEX presence are presented in Church et al. (1999) and Koenigsberg et al. (1999). Deeb et al. (2001) reported that when PM1 cells were grown on MTBE, if presented a mixture of MTBE + benzene and MTBE + toluene, MTBE degradation occurred first, and degradation of the aromatics lagged for 4 h (a shorter lag than when benzene was present alone). After the lag, the aromatics were degraded rapidly, and the rate of MTBE degradation declined. Once the aromatics were degraded, the MTBE degradation rate increased to its earlier rate. When PM1 was grown on benzene, MTBE degradation had a long lag phase, but benzene degradation did not. The authors hypothesized that BTEX and MTBE are degraded by two different inducible metabolic pathways.

In addition, MTBE biodegradation via cometabolism by alkane oxidizers has been studied. Hardison et al. (1997), Steffan et al. (1997), Hatzinger et al. (2001). Garnier et al. (1999), and Hyman et al. (1998) all reported on cometabolic degradation of MTBE using *n*-butane, propane, *n*-pentane, *h*-hexane, isobutane, and isopentane substrates.

Finally, some researchers have reported biodegradation of MTBE under anaerobic conditions. Studies that show evidence of anaerobic MTBE biodegradation include Mormile et al. (1994), Finneran and Lovley (2001) (iron reduction), Yeh and Novak (1994) (methanogenic), and Bradley et al. (2001a) (nitrate and sulfate reduction). Additionally, Wilson et al. (2000) studied MTBE biodegradation under methanogenic conditions in microcosms containing either MTBE only or MTBE plus alkylbenzenes. In the MTBE + alkylbenzenes treatment, MTBE did not degrade until the alkylbenzenes were completely removed. In the MTBE only treatment, MTBE decreased in the live microcosms up to three orders of magnitude. It could not be determined whether the alkylbenzenes interfered with MTBE degradation. Coversely, Bradley et al. (1999) saw no mineralization of uniformly labeled ^{14}C-MTBE in streambed sediments under strict anaerobic conditions, but the microcosms did produce methane; Landmeyer et al. (1998) saw no mineralization of MTBE after 7 months of incubation under iron-reducing conditions, and Bradley et al. (2001a) did not observe MTBE biodegradation under methanogenic conditions and limited mineralization under iron- and manganese-reducing conditions at one site.

In summary, it has been clearly established that MTBE degrades, by both mixed cultures and pure cultures, under aerobic conditions. In general, slow growth has been observed (Salanitro et al. 1994), but organisms, such as PM-1 (Hanson et al. 1999), are being discovered that have more rapid growth on MTBE. In some situations, the addition of a cosubstrate has resulted in MTBE biodegradation (Steffan et al. 1997; Hardison et al. 1997). While there are reports of anaerobic biodegradation of MTBE, it is likely that aerobic biodegradation will prove to be the remedy chosen for quick remediation of contaminated sites.

Methyl *tertiary*-Butyl Ether Remediation

Deeb and Kavanaugh (2001) and Brown et al. (1997) discussed potential technologies for MTBE treatment. Among the technologies presented by the authors are advanced oxidation processes (ozone, UV, and hydrogen peroxide addition), adsorption, membrane separation, air stripping, pump-and-treat, and soil vapor extraction. The majority of these technologies are ex-situ treatment methods requiring the removal of contaminated soils or groundwater. In situ bioremediation, and monitored natural attenuation, on the other hand, do not involve the transfer of contamination among the different media. The remainder of this section will focus on advances made in natural attenuation assessments and in situ bioremediation for MTBE plumes.

In Situ Bioremediation

There are three main strategies being used to aid MTBE biodegradation at contaminated sites. The first strategy is a result of the successful aerobic biodegradation of MTBE in the laboratory. Oxygen is added to encourage more rapid in situ biodegradation. Because some laboratory studies have shown the heterogeneous distribution of MTBE-degrading organisms, [e.g., only one replicate of Mormile et al. (1994), Yeh and Novak (1994), Hunkeler et al. (2001), and Finneran and Lovley's (2001) studies of MTBE degradation showed evidence of biodegradation], another approach is to augment a field site with microorganisms that are adapted to MTBE. Lastly, a cosubstrate may be added to promote biodegradation of MTBE. The addition of microorganisms and the addition of a cosubstrate both have their critics. Rather than add microorganisms, it has been argued that the addition of oxygen should be sufficient because the necessary organisms are present and just need time to adapt, if they are not already adapted. As for adding propane or other alkanes, the criticism with this approach is that adding propane increases the oxygen demand and, therefore, costs.

Successful biodegradation of MTBE in areas of a site where oxygen was added was reported by Javanmardian and Glasser (1997) and Koenigsberg et al. (1999). The latter observed biodegradation of MTBE at the site of a leaking underground storage tank in Lake Geneva, Wis. after injection of Oxygen Release Compound (ORC, a slurry of magnesium peroxide, Regenesis, San Juan Capistrano, Calif.) as a slurry to provide oxygen. Their results were confirmed by Landmeyer et al. (2000), who concluded that addition of ORC at their study site (rather than additon of oxygen and microorganisms) was sufficient for degradation of MTBE.

At Vandenberg AFB, pilot tests with oxygen addition were also conducted by Mackay et al. (1999). In one pilot test, release wells (tubing source emitters) for release of oxygen and other gases were studied. Another pilot test was of a release panel, which uses a flat, permeable panel to house emitter tubing, and a third test was conducted of the diffusive tubing emitters (Wilson et al. 2002) in a longitudinal test facility (LTF). The DO of the anoxic water entering the LTF was raised to 15–23 mg/L. The pseudo first-order MTBE degradation rate was estimated at $5.3 + 0.1\ \text{day}^{-1}$. If oxygen addition ceased, downgradient concentrations of MTBE rose to match the upgradient concentrations, indicating that the oxygen was being used for biodegradation. The authors noted that more oxygen was used than was needed to satisfy the oxygen demand of MTBE, and they speculated that reduced minerals and other organics exerted the additional oxygen demand.

Another in situ bioremediation strategy is the addition of microorganisms capable of degrading MTBE. The consortium MC-100 [formerly BC-100, Salanitro et al. (1994)] was used in a field test of biostimulation and bioaugmentation at the SERDP-U.S. Navy National Environmental Test Site at Port Hueneme, Calif. Results suggest that augmentation with MTBE degraders will more rapidly reduce MTBE concentrations and reduce them to lower concentrations than adding oxygen alone. This bioaugmentation process, now referred to as BioRemedy, was also used at two service stations, one in California and one in Connecticut (Spinnler et al. 2001a,b). The MTBE-degrading microbial culture is added to the subsurface near the leading edge of a MTBE plume, and oxygen gas is pulsed into injection wells. At the northeastern site, MTBE concentrations dropped by two to three orders of magnitude after 6 months; the authors attributed the degradation to the added culture. At the California site, MTBE concentrations had declined from about 20 mg/L to low ug/L levels after 1 year of operation.

In a later field test at Port Hueneme, the biodegradative activity of the mixed culture MC-100 and the pure culture SC-100 (*Rhodococcus* sp. nov) is being compared (Salanitro et al. 2001). Gas and microbes were added from 7.6 to 9.1 m (25 to 30 ft) downgradient of the ''beginning'' or inlet of the biobarrier. Monitoring wells were installed within the biobarrier and up- and downgradient at two depths. The authors observed that MTBE concentrations in the shallow monitoring wells declined from 1–3 mg/L upgradient to 10 ug/L in the seeded zone in all three test plots 64 days after inoculation and then declined to <1 ug/L after 173 and 275 days. MTBE concentrations did not decline as rapidly or to the same extent in the deep monitoring wells, possibly as a result of a slower start in aeration/oxygenation.

Envirogen conducted the first application of in situ cometabolic degradation at a service station in New Jersey by adding propane plus microorganisms (Steffan et al. 2001, 2002). At this site, MTBE and BTEX were both present, at an average concentration of 100 and 1 mg/L, respectively. The site underwent air sparging for approximately 6 months, which reduced concentrations of BTEX but not MTBE. Microcosm experiments investigated the biodegradability of MTBE at the site (Steffan et al. 2002). Addition of oxygen or oxygen plus propane to the microcosms did not promote biodegradation. Addition of the propane-oxidizing bacterium ENV 425, along with propane and oxygen and adjustment to neutral pH led to biodegradation of MTBE in the microcosms. At the field site, air was added continuously and propane was added as 0.2% propane in air for 10 min duration every 3 h. The system was operated in this manner for 1 month and then 17 L of the culture ENV425 was added to the three sparge wells. After 5 months, the furthest downgradient well did not show any effects from the treatment; the three other wells, however, experienced declines in MTBE concentration during system operation, and propane was not detected in any of the wells during the treatment phase. The authors state that the changes in MTBE concentration were not due to seasonal variation in MTBE concentration and included pretreatment MTBE concentration data.

Natural Attenuation

While in situ bioremediation shows promise for MTBE removal, much research remains to be done about its viability as a cost-effective technology. This fact combined with the increased use of natural attenuation for remediating low-risk BTEX plumes led researchers to study the natural attenuation of MTBE plumes. A number of studies have been completed to date, including studies at Base Borden, Sampson County site, Elizabeth City site, 74 Amoco service stations, and the Laurel Bay Exchange site. The results from these sites are encouraging regarding the prospects for using natural attenuation for MTBE remediation.

In a chloride tracer and oxygenated gasoline injection test at Canadian Forces Base Borden in Ontario, Canada in the late 1980s, the migration of BTEX and MTBE was monitored for 16 months. The BTEX mass of the gasoline declined dramatically during the monitoring period, but the MTBE/Cl^- mass ratio declined only slightly, from 0.59 initially to 0.43 (Hubbard et al. 1994). Because the mass balance was uncertain, degradation of MTBE could not be demonstrated. In 1995–1996, additional sampling was conducted to determine the fate of the MTBE plume (Schirmer and Barker 1998). According to numerical modeling, maximum MTBE concentrations should have been greater than 3 mg/L if no degradation occurred, and the plume should have traveled 240 m (790 ft). The sampling program found maximum concentrations of MTBE below 0.2 mg/L. MTBE was detected only at the deepest sampling points, closest to the aquitard. Detection of MTBE coincided with sulfate concentrations greater than 10 mg/L and dissolved oxygen less than 1.8 mg/L. However, a boundary between the background groundwater and the existing landfill leachate plume could not be determined. After accounting for the mass of MTBE in the aquifer, it was found that only 3% of the original mass remained. The authors concluded that the MTBE mass was most likely lost through natural attenuation.

A field study of natural attenuation was conducted at an underground storage tank release site in Sampson County, N.C. (Borden et al. 1997). Four lines of multilevel wells were installed across the plume (line 1 at the source and line 4 the furthest from the source). The authors observed that there was degradation of MTBE near the source but not at the furthest downgradient wells. The mass flux of toluene, ethylbenzene, and m/p-xylenes decreased by 99% between the source (line 1 wells) and the line 3 wells, a distance of 88 m (289 ft), between 1994 and 1995. The mass flux of o-xylene, benzene, and MTBE decreased by 89, 87, and 74% over the same distance and monitoring period. The average first-order decay coefficient was calculated for each compound between well line 1 and 2, line 2 and 3, and line 3 and 4. At the source (between line 1 and 2), the decay coefficient ranged from a high of 0.0063 day^{-1} for toluene to a low of 0.0010 day^{-1} for MTBE. Downgradient, the decay coefficients decreased. For example, toluene's decreased to 0.0005 day^{-1}. At line 4, there was >100 ug/L of o-xylene, benzene and MTBE remaining, and there was also a decrease in their decay coefficients (0 for MTBE). As the authors state, the spatial relationship of decay coefficients is very significant. If the source area decay coefficient was used as the coefficient for the entire site, the amount of contaminant transport, and therefore risk, would be underestimated.

Wilson et al. (2000) reported on natural attenuation at a fuel farm site in Elizabeth City. High concentrations of TPH and MTBE were located 1.5–3 m (5–10 ft) below ground surface. At this site, it did not appear that there was any difference in the plumes (and pattern of degradation) of MTBE and BTEX. A plume of methane was detected (average concentration 7 mg/L), and it coincided with the plume of MTBE. Dissolved oxygen was absent in the source area, and there was evidence of sulfate and iron reduction processes [sulfate depletion and Fe(II) production in the contaminated areas]. The rate of disappearance of MTBE in the field was determined for three different groundwater seepage velocities. At the upper limit, the MTBE degradation rate was 5.0 per year, 2.7 per year, and 2.2 per year at the lowest velocity. They determined the rate of natural attenuation of the source area by comparing the flux of MTBE moving away from the source to the total mass of MTBE in the source area. The flux of MTBE in 1996 was 2.76 kg/year, and the mass of MTBE in the source was at least 46 kg. Since the MTBE average concentration in the source was 1,200 μg/L, it would take 60 years for the concentration to reach 30 μg/L.

BP Amoco, Handex Environmental, and the EPA conducted a groundwater sampling survey at 74 gasoline stations in the United

States, looking at natural attenuation of BTEX and MTBE. Methane was used as a tracer. The groundwater samples were also analyzed for TBA, trimethylbenzene, and geochemical parameters such as DO, dissolved methane, ethane, propane, and butane, Fe II, TOC, sulfate, nitrate, alkalinity, and pH (Kolhatkar et al. 2000). In this study, the concentrations of MTBE were normalized by dividing by the methane concentration. The natural logarithms of the concentrations were regressed with travel time to get a first-order biodegradation rate constant (the slope of the regression line). Using this approach, biodegradation rate constants were determined for 6 of the 74 sites. The MTBE degradation rates range from 0.3 to 10.9 per year, similar to the benzene rates. The authors found that MTBE degradation was associated with strongly methanogenic sites, not weakly anoxic ones.

Kolhatkar et al. (2001) further conducted a detailed study at one of the Amoco study sites. After excavating the soil at this Long Island, N.Y. site, dual-phase extraction was conducted, followed by an air sparging/SVE system that is currently in operation. Sampling showed that the MTBE plume descends deeper as it travels downgradient. Methane was present in the shallow downgradient wells where MTBE was absent, and the methane plume was much more confined vertically during this study's two sampling events. Using the shallow well data, a first order biodegradation rate constant for MTBE was calculated to be 5.2 year^{-1}. The downgradient extents of both plumes appear to be undefined ($>$1,000 ug/L MTBE at most downgradient well, $>$0.5 mg/L methane). Sulfate concentrations are high ($>$25 mg/L) in the deeper portion of the plume. The authors state that the MTBE is being biodegraded in the shallow, methanogenic groundwater. Alternatively, it is possible that the MTBE plume is being driven down by seasonal recharge [an observation also reported by Landmeyer et al. (1998) and Borden et al. (1997)]. Kolhatkar et al. (2001) offer no mechanistic explanation for why MTBE would be degraded in a methanogenic zone, yet persist in the aerobic zones. Currently, in the literature, there is very little evidence for MTBE biodegradation under methanogenic conditions [only in one soil type in Yeh and Novak (1994), after 270 days' incubation, some apparent degradation in the methanogenic microcosms of Wilson et al. (2000)]. However, the authors are conducting detailed microcosm studies to investigate the biodegradation of MTBE under different redox conditions using material from this site. The preliminary results indicate that there is methanogenic biodegration of MTBE at this site (Kolhatkar, personal communication 2001).

Finally, natural attenuation of MTBE using data collected over a 5-year period was reported in a USGS study at Port Royal Island, Laurel Bay Exhange, MCAS Beaufort, S.C. (Landmeyer et al. 1998). MTBE was detected in downgradient wells before benzene, and higher concentrations of MTBE and benzene were detected in deeper-screened intervals of the multilevel wells than in the shallow intervals or in the conventional monitoring wells. The detection of MTBE and benzene at deeper sampling zones suggested to the authors that recharge is displacing these plumes deeper into the aquifer. This phenomenon has important implications for risk assessment when using conventional, water-table screened monitoring wells. The benzene and MTBE plumes were wider where groundwater flow was slow and narrower where flow rates were high. There was questionable biodegradation of MTBE in concomitant microcosm studies using uniformly labeled ^{14}C-MTBE, because less than 3% was evolved as $^{14}CO_2$ after 7 months of incubation. Intermediates of MTBE degradation were not analyzed. This lack of mineralization is probably responsible for the relatively high levels of MTBE that remained in the aquifer. In this aquifer, the processes of dilution and dispersion were likely to be responsible for the observed decreases in MTBE concentration relative to benzene. Attenuation of MTBE through dispersion and dilution is the same mechanism proposed by Happel et al. (1998) in their study of UST sites in San Diego County, Calif.

Summary and Conclusions

In summary, promising results have been seen with all the approaches to bioremediation of MTBE in the field. MTBE degradation has been observed with oxygen addition, bioaugmentation, and addition of propane as a cosubstrate. It is too soon to say which approach is superior, and it is likely that the best approach will depend on the conditions of the field site. Future field tests, such as those that are occurring at Port Hueneme's National Environmental Test Site, will provide more information about MTBE remediation methods. Evidence is mounting for natural attenuation at field sites, and it is probable that as better methods evolve to study MTBE concentrations in the field, in particular, the use of carbon isotope fractionation, investigators will be better able to differentiate sites where natural attenuation is sufficient from those that require more intervention to avoid adverse outcomes. Clearly, though, now that our understanding of MTBE biodegradation is increasing, with respect to groundwater contamination, the situation appears less dire than earlier predictions would have led one to believe.

Practically speaking and as mentioned previously, many states have and will opt out of using MTBE and seek other alternatives for fuel efficiency. One of the alternatives to MTBE is the use of ethanol. Ethanol is already the most commonly used oxygenate in the Wintertime Oxyfuel program (USEPA 2000), but production would need to be increased to meet this new demand. States that use MTBE-containing gasoline will likely see an increase in price from between 2.4 and 3.9 cents per gallon (USEPA 2000). Because ethanol will separate from gasoline in pipelines, it must be blended with gasoline at the terminal. Terminals will then need storage areas for ethanol. Storing ethanol inevitably leads to the prospect of an ethanol spill or release to the subsurface. In the case of a pure ethanol spill, such as might occur at a terminal, the resulting high concentrations of ethanol could lead to order-of-magnitude increases in BTEX concentrations in groundwater (Powers et al. 2001). In the range of aqueous phase ethanol concentrations from reformulated gasoline, benzene, toluene, and xylene concentrations generally increase by only 20–60%.

Another reason for caution in the use of ethanol as an additive is that ethanol is a highly biodegradable substance and will be preferentially degraded before the regulated, aromatic components of gasoline (benzene, toluene, ethylbenzene, and xylenes, or BTEX). Its biodegradation will rapidly drive a source zone anaerobic. BTEX plumes will probably grow longer if ethanol is part of the mix than they would otherwise. Several modeling studies suggest that benzene plumes will grow 20–150% longer from an ethanol-blended gasoline spill than they would from a nonoxygenated gasoline (Powers et al. 2001). Further research will be needed to evaluate the environmental impacts of replacing MTBE with other alternatives such as ethanol.

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