



TechData Sheet

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Methyl Tertiary Butyl Ether (MTBE) Bioremediation

Introduction

M*ethyl tertiary butyl ether* (MTBE) is an oxygen-containing gasoline additive. It has been used in the United States since the late seventies, with usage increasing steadily in the eighties. Usage increased dramatically in the nineties following passage of the 1990 Clean Air Act. Under the Clean Air Act, the Environmental Protection Agency (EPA) issued regulations that require gasoline to be “reformulated” in order to significantly reduce vehicle emissions of ozone-forming and toxic air pollutants. (Reformulated gasoline (RFG) contains 11% MTBE.) MTBE is the most commonly used gasoline additive and the second most manufactured chemical in the United States.

MTBE is present in the environment due primarily to gasoline losses from leaking underground storage tanks (LUSTs). Of 6,127 LUST sites tested in California, 4,595 or 75% of the sites contained MTBE (based on groundwater data collected between 1995 and 1998). From 5 to 10% of drinking water wells in RFG/Oxy-fuel areas detected MTBE, although most (99%) detections were less than 20 µg/L. MTBE in drinking water sources is of concern because MTBE has low taste and odor thresholds (20 to 40 µg/L) that can make a water supply nonpotable even at low concentrations.

Regulatory Concerns

There is no enforceable federal drinking water regulation established for MTBE. Standards vary from state to state, as shown in Table 1.

Table 1. Recent Water Standards for MTBE

Locale (year)	MTBE Standard (µg/L)	Type of Water Standard
Federal (1998)	20 - 4	Health advisory (HA) for taste and odor; nonenforceable
California (1999)	13 - Maximum Contaminant Level (MCL) (expected)	Drinking water; enforceable
New York (1999)	5 - Suggested MCL 10	“Guidance criteria” enforceable for all waters; stringent

An EPA Blue Ribbon Panel recently issued a report that advised “the use of MTBE should be reduced substantially.” A 1999 New England study advised a 3-year phase down and cap on MTBE. California has banned MTBE use after December 2002. Several states and air quality non-attainment areas are trying to get out of the Federal RFG and Oxy-fuel programs, mostly to help avoid MTBE.

Class-action lawsuits about MTBE usage have been filed against oil companies, gasoline distributors, and MTBE manufacturers in several states, including Maine, North Carolina, New York, and California.

Traditional Remediation Technologies

MTBE is 28 times more soluble than benzene, but 10 times less volatile from water than benzene. MTBE plumes usually

move faster and farther than benzene, toluene, ethylbenzene, and xylene (BTEX) compounds. MTBE plumes occasionally source separate, or detach, and sometimes MTBE plumes extend deeper into aquifers (i.e., “dive”), especially on the leading edge.

Many technologies that work for remediating gasoline will also work for MTBE. However, most will be less effective and/or more costly for MTBE. Table 2 summarizes the information available on some of the traditional remediation technologies that have been used for sites contaminated with MTBE.

Table 2. Traditional Remediation Technologies

Technology	Applicability for MTBE	Reported Field Applications	Performance and Comments
RBCA approach	Fully applicable	Few	Process works fine, but results maybe unfavorable for MTBE.
Soil vapor extraction (SVE)	Very applicable	Dozens	MTBE's high vapor pressure makes SVE excellent initially; but only before MTBE leaches into groundwater.
Ground-water extraction	Plume control is very good	Dozens	Pump and treat is great for hydraulic containment; still limited by residual product and hydrogen.
	Remediation is good for dissolved phase	Dozens	Better for soluble MTBE than for most compounds.
Soil extraction	Variable with time	Few	If implemented soon after spill, can be effective; if implemented later, when the MTBE is leached from soil, is ineffective.
Air sparging	Variable, still being determined	> 12	Aeration benefit reduced (hard to “strip”O and biodegradation benefit much reduced; field results mixed from good to very poor.
Bioventing	Not promising so far	3 - 4	Performance poor; so far control areas show no measurable improvement.

Table 3 summarizes the effectiveness of aboveground treatment methods for MTBE-impacted water.

Innovative Remediation Technologies

Several innovative remediation technologies have been proposed for MTBE. **Phytoremediation** uses the evapotranspiration of plants and trees to decontaminate the subsurface. For MTBE phytoremediation depends primarily on mass removal to control the downgradient spread of dissolved-phase MTBE. Cores of live oak trees above a plume showed MTBE in the tree fluids. Some field tests are ongoing at MTBE sites; however the technology is still developing. **In-situ oxidation** is a technology that uses hydroxyl radicals (OH

Table 3. Aboveground Treatment of MTBE Impacted Water

Technology	Theoretical Effectiveness on MTBE	Development Level	Performance and Comments
Air stripping	Good - fair	Field; many good applications	Higher air/water ratio needed; air emissions problematic.
Carbon adsorption	Good in selected situations	Field; some good applications; many poor ones	High granular active carbon usage (rapid breakthrough possible); virgin coconut GAC best.
Advanced oxidation processes	Good	Pilot looks promising; field studies starting	Destroys MTBE; high capital costs; byproducts can be problematic.
Resin sorbents	Good; effective on TBA	Lab; pilot test starting	Looks promising, especially if TBA is present and of concern; high capital costs.

groups) created in the ground by Fenton’s reaction. These radicals can destroy MTBE. The process requires the subsurface injection of ozone, H₂O₂, or both.

Bioremediation has been effective for a number of other contaminants, including BTEX. MTBE is more difficult to biodegrade than other compounds for a number of reasons, including:

- **Chemical structure** – MTBE is an ether with a tertiary carbon bond (difficult to break bonds).
- **Cell growth** – slow growth (0.05/day) with low yield (0.1-0.2 g-cells/g-MTBE).
- **Population** – low number of indigenous degraders (0.001% of total population in biotreaters).
- **MTBE-degrading activity** – most cultures are aerobic and are affected by low dissolved oxygen (DO), low pH, and temperature.
- MTBE does not degrade well in the presence of more readily consumed compounds like BTEX.
- For large, dilute plumes, MTBE concentrations may be too low to support rapid bioactivity.

Some of these factors can be overcome. Figure 1 (Dr. Joseph P. Salanitro, Equilon Ent. LLC) shows the results of adding dissolved oxygen to an experimental microcosm. Figure 2 (Dr. Joseph P. Salanitro, Equilon Ent. LLC) shows the results of adding MTBE degrading microorganisms to an experimental microcosm.

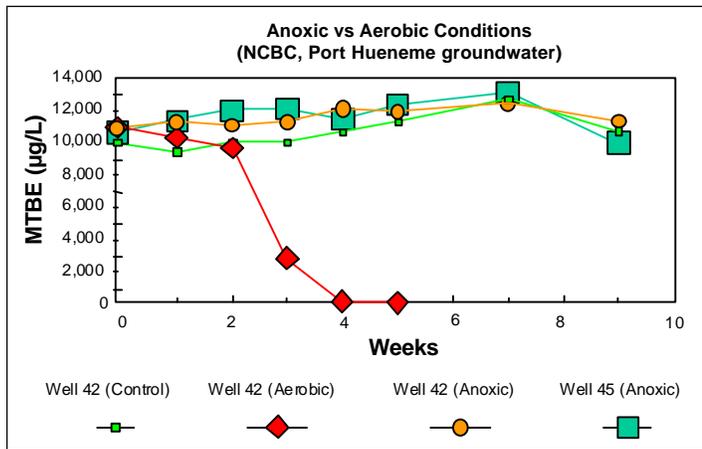


Figure 1. Experimental microcosms - no microbial cultures added.

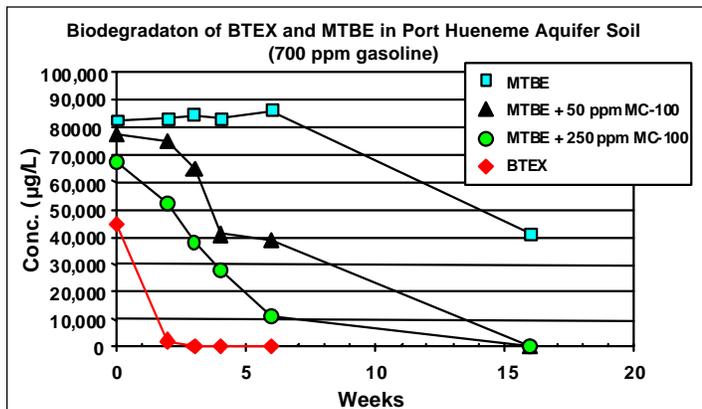


Figure 2. Experimental microcosms - microbial cultures added.

Biobarrier Field Test, Port Hueneme, California

A biobarrier field test was conducted at NCBC, Port Hueneme, California. At this site, the MTBE plume was more than 4,000 feet long. The treatment plot was situated in an MTBE only portion of the plume, with MTBE concentrations ranging from 2 to 9 µg/L and a plume thickness of 10 feet. DO was less than 1 µg/L the depth to water was approximately 10 feet.

This enhanced biodegradation technology involved three main steps:

1. Oxygenate (by pure oxygen injection)
2. Inoculate with MTBE-degraders (MC-100)
3. Monitor

Intermittent sparging with pure oxygen started 6 weeks before microbial seeding and succeeded in raising DO levels from about 1 µg/L up to 10 to 20 µg/L. Thirty-two days after seeding with MC-100, MTBE levels immediately downgradient dropped 90%. By day 261 in the treated plot, MTBE was not detectable in many sample locales, with 10 to 50 µg/L in a few locales. The O₂ only plot did show some MTBE decreases, apparently due to enhanced natural biodegradation processes after some lag time.

The in-situ MC-100 biobarrier appears capable of degrading MTBE to <5 µg/L, without TBA residuals and the microbial activity remains to at least 261 days. The combination of bioaugmentation with adding oxygen appears to be a feasible in-situ MTBE biotreatment option.

Case Study – La Crosse, Kansas

Although the spill history is unknown, an aquifer in Lacrosse, Kansas, was impacted by MTBE-blended gasoline sometime in the last 10 years. Public water supply is from several production wells in a sole-source aquifer. In May 1996, a resident noticed a strange odor in an irrigation well. Sampling of an adjacent public well detected MTBE at 200 µg/L. Detailed assessment (by 60 monitoring wells) showed that the MTBE had migrated beneath an 800-foot long, 2-D shallow monitoring system, entered the valley fill aquifer, and impacted the public well field 4,000 feet away.

Source area remediation was conducted, including soil excavation, soil vapor extraction (SVE), air sparging, and a barrier of oxygen release compound (ORC), all with limited effectiveness. Two impacted public wells were pumped at a total flow rate of 300 to 450 gpm to contain and extract the contaminated groundwater.

In September 1997, two air strippers were installed at the water treatment plant (see Figure 3). Each was 6 feet in diameter, with 30 feet of 2-inch Jaeger tripacks. The strippers were operated in series, each with an air-to-water ratio of 175:1. Each tower removed 80 to 90% MTBE. With influents of 200 to 600 µg/L, treated water ranges from non-detect to 24 µg/L. This simple and logical application of traditional technologies restored public water usage, and controlled the MTBE plume.

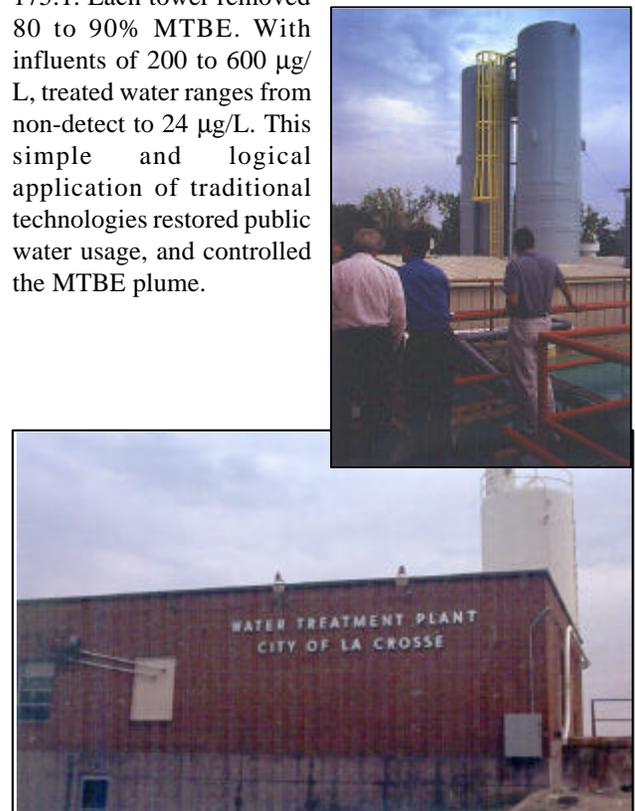


Figure 3. Case study: La Crosse, Kansas.

Cost

- The added cost of remediating a gasoline spill site when MTBE is present varies widely:
 - ◊ If active remediation is ongoing, then a little MTBE arrives, and no system changes needed ⇒ little to no cost increase.
 - ◊ If active remediation is ongoing, then MTBE arrives, and system changes or expansion are needed ⇒ moderate cost increase
 - ◊ If active remediation is not occurring, then MTBE arrives, and a new remedial method is needed (i.e., change from passive to active) ⇒ major cost increase
- Cost of treating MTBE-impacted water has been estimated at 40 to 80% more than treating BTEX-impacted water (Keller et al., 1999)
- Survey of early MTBE experience in RFG states (Hitzig, et al., 1998) concluded how the presence of MTBE impacts the total cost of remediation:
 - ◊ At 60% of LUST sites, cost increases due to MTBE are 0 to 20%.
 - ◊ At 32% of LUST sites, cost increases due to MTBE are 20 to 100%.
 - ◊ At 8% of LUST sites, cost increases due to MTBE are >100%.
- “Hot spot” reduction, a quick response, and/or using alternative cleanup goals can greatly reduce the scale of a remedial project, thus saving money.

Conclusions

1. Increasing regulatory and litigation activity indicates that MTBE contamination may become a bigger concern.
2. Be attentive when defining MTBE plumes (they can move fast and far; they can dive).
3. Most traditional technologies are applicable to MTBE, though often less effective than for BTEX.
4. Many MTBE plumes will be more difficult or more costly to remediate than BTEX plumes.
5. Several innovative technologies look promising, especially enhanced bioremediation.
6. Field experience has shown that subsurface MTBE contamination can be remediated and treated.
7. MTBE may cause active remediation costs to increase 20 to 80% at many sites, and significantly more at some sites.

References

- Hitzig, et. al, “Study reports LUST programs are feeling effects of MTBE releases,” Aug 1998.
- Keller, A. A.; O. C. Sandall; R. G. Rinker; M. M. Mintani; B. Bierwagen; and M. J. Snodgrass. “An evaluation of physicochemical treatment technologies for water contaminated with MTBE,” 1999.

**For more information on MTBE remediation,
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