



MTBE Fact Sheet #2

Remediation Of MTBE Contaminated Soil And Groundwater

Background

Methyl tertiary-butyl ether (MTBE) is a fuel additive made, in part, from natural gas. Since 1979, it has been used in the United States as an octane enhancing replacement for lead, primarily in mid- and high-grade gasoline at concentrations as high as 8 percent (by volume). Since the mid-1980s, it has been widely used throughout the country for this purpose. It is also used as a fuel oxygenate at higher concentrations (11 to 15 percent by volume) as part of two U.S. EPA programs to reduce ozone and carbon monoxide levels in the most polluted areas of the country.

Physical And Chemical Characteristics Of MTBE

The effectiveness of remediation methods is directly linked to the physical and chemical characteristics of the constituent of interest. Because MTBE behaves differently in soil, air, and water than other petroleum constituents, the choice of an effective remediation technology may be different when

MTBE is present at a site. Benzene is most often the contaminant of concern in gasoline because of its relatively high solubility and its known carcinogenicity. As a result, comparing the characteristics of MTBE with benzene is helpful in showing how remediation technologies may differ when MTBE is added to gasoline.

- # MTBE is about 30 times more soluble than benzene in water. Pure MTBE can reach an equilibrium concentration in water of approximately 5 percent (*i.e.*, 48,000 mg/L).
- 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 ten times less volatile than benzene (*i.e.*, its Henry's law constant is 1/10th benzene).

- MTBE is much less likely than benzene to adsorb to soil or organic carbon.
- MTBE is more resistant to biodegradation than benzene.

When MTBE is in the soil as the result of a petroleum release, it may separate from the rest of the petroleum, reaching the groundwater first and dissolving rapidly. Once in the groundwater, MTBE travels at about the same rate as the groundwater whereas benzene and other petroleum constituents tend to biodegrade and adsorb to soil particles.

Soil Remediation

Because it has a very high vapor pressure and a low affinity for sorption to soil, MTBE can be effectively remediated by two soil treatment technologies, typically without any costs beyond those needed for remediating other petroleum constituents. Soil vapor extraction (SVE) is an *in situ* soil treatment technology that removes volatile contaminants from soil in the unsaturated zone above groundwater by extracting the contaminant vapors with a vacuum that is applied to the subsurface. Low-temperature thermal desorption (LTTD) is an *ex situ* soil treatment technology that uses temperatures below ignition levels to separate volatile contaminants from soil. Because of its high vapor pressure, both methods are very effective in removing MTBE from soil. However, SVE and LTTD must be used soon after a release, before most of the MTBE moves from the soil into the groundwater.

Bioremediation methods for soil treatment (*e.g.*, land-farming, bioventing, biopiles) are currently not recommended for removing MTBE because it is

considered recalcitrant to biodegradation. This recommendation may change in the future as new research examines the efficacy of specific strains of bacteria and/or improved methods of biodegrading MTBE.

Groundwater Investigations And Monitoring

Because MTBE behaves differently from petroleum hydrocarbons when released into the environment, a remedial investigation may need to be modified to properly characterize the area of MTBE contamination. Many regulators of UST programs have observed that MTBE's relatively high solubility allows it to dissolve into the groundwater in "pulses" that result in rapid orders of magnitude changes in groundwater concentrations. Pulses, which may be caused by the infiltration of rain water or rising groundwater levels, may necessitate frequent groundwater sampling to determine actual MTBE concentrations and levels of risk to down-gradient receptors. The frequency of sampling should be determined based on the velocity of the groundwater and the number of monitoring wells. Determining the impact of the selected remediation method may be difficult without accurate historical sampling data.

Groundwater Remediation

Pump-And-Treat

In contrast with the preferred remediation techniques for petroleum hydrocarbons such as benzene (*e.g.*, bioremediation), pumping contaminated groundwater and treating it above

ground (*i.e.*, pump-and-treat) may more often be an effective remediation technology for MTBE because MTBE does not adsorb significantly to soil. As a result, fewer aquifer volumes are required to remove all of the MTBE than are required to remove the slowly desorbing petroleum hydrocarbons. In addition, because it is highly soluble, most of the MTBE mass may quickly dissolve into groundwater, making pumping an efficient method for removing large quantities of the contaminant.

As with petroleum hydrocarbons, however, diffusion is also a factor controlling the remediation timeframe. If micropores exist within the aquifer that are not readily influenced by groundwater flow, transfer of a contaminant from the micropores to the macropores will occur through the slow process of diffusion. Hence, in spite of some favorable characteristics, pump-and-treat may not always be an efficient remediation method for MTBE contamination. Aquifers with high total porosity but with low effective porosity remain troublesome in treating any contaminant.

The physical and chemical properties of MTBE are also important in the treatment of MTBE above ground. Because it does not adsorb significantly to carbon, MTBE is not a good candidate for using granular-activated carbon (GAC) to remove it from water. GAC is about 1/3 to 1/8 as effective in removing MTBE as it is in removing benzene. In addition, because MTBE “prefers” to remain in water, air strippers must use a higher volume of air than is required for benzene. Initial field experience indicates that two to five times more air is needed to treat the same volume of water if MTBE

concentrations are less than 5,000 ppb. An additional expense associated with MTBE remediation is that more extraction wells and associated equipment (*e.g.*, pumps, lines) may be required than for benzene because MTBE travels farther and faster than the rest of the plume, resulting in a larger plume size.

The cost of treating an MTBE groundwater plume can be significant, however, cost effective methods do exist. A 1991 American Petroleum Institute study (API Publication No. 4497) determined that air stripping alone was the most cost effective technology for remediating water containing 20-ppm MTBE down to a level of 10 ppb. A 25-gallon per minute air stripping system could achieve this level of remediation for \$9 per 1000 gallons (in 1990 dollars). If off-gas emissions were also a concern, they could be treated for an incremental cost increase of \$7 per 1000 gallons (*i.e.*, \$16 per 1000 gallons total cost). As an alternative, UV-catalyzed oxidation using hydrogen peroxide could be used to treat water and off-gases at a total cost of \$15 per 1000 gallons.

Air Sparging

Air sparging is another groundwater remediation technology that has shown some promise. It accomplishes remediation goals by injecting air directly into the groundwater to volatilize the contaminants *in situ*. A few case studies have shown that reductions in MTBE levels from above 1000 ppb to less than 10 ppb are possible in less than 2 years. However, regardless of the contaminant, air sparging is typically only appropriate in homogeneous sands because heterogeneous sediments may cause dispersion of contaminants and

channeling of air flow. In addition, air sparging should be less effective for MTBE than for benzene because more air is needed to volatilize the MTBE. The addition of dissolved oxygen in the groundwater from air sparging may not significantly increase the biodegradation of MTBE as it would for benzene.

Bioremediation

Although MTBE is generally believed to be resistant to biodegradation, preliminary research has shown that biodegradation may be an effective remediation option under specific conditions. Bioreactors, an *ex situ* form of bioremediation, have shown some initial promise. Additional research and development are continuing to make them more reliable and cost effective. New research is also showing that *in situ* biodegradation may be an effective remediation alternative; however, more information is required to determine the specific environmental conditions that enable significant rates of biodegradation to occur.

Point-Of-Use Treatment

Because MTBE groundwater plumes commonly travel farther than benzene plumes, MTBE may be more likely than the remainder of the petroleum release to impact drinking water wells. As a result, many states have been treating contaminated groundwater at the point of exposure and at the source area of the plume. In New Jersey, regulators have found that GAC is effective in treating low-volume potable wells (*e.g.*, for single-family homes) with contamination levels below 300 ppb. If high-volume potable wells are involved (*e.g.*, for restaurants,

industrial sites) or if concentrations exceed 300 ppb, miniature air strippers may be a more cost-effective option. Manufacturer specifications should be consulted for any treatment unit and followed up with adequate levels of influent and effluent monitoring.

Incremental Cost Increase Of MTBE Groundwater Remediation

The incremental cost increases for UST corrective action activities that involve MTBE versus ones that do not contain MTBE vary widely depending on the history of the release (*e.g.*, how long the release has been occurring, whether MTBE was contained in the initial release, the concentration of MTBE) and the goals of the cleanup. At many sites, the initial concentrations may be low enough that MTBE may not be a greater concern than the remediation of benzene, resulting in no cost increase. But, when an MTBE plume is much larger than the benzene plume and impacts drinking water wells ahead of it, MTBE will be the driving force in remediation efforts, potentially resulting in a very high incremental cost increase.

Based on limited research and anecdotal information, the U.S. EPA's Office of Underground Storage Tanks estimates that at approximately 75 per-cent of MTBE-contaminated sites, the incremental cost increase of remediation will be less than 50 percent above the cost of remediating the same petroleum release without MTBE. At many of these sites, costs would actually not increase because benzene might still pose the greatest risk, thus driving the remediation effort. At 20 percent of the sites, the incremental cost increase would be between 50

percent and 100 percent. At the remainder (approximately 5 percent) of the sites, the additional cost of remediating MTBE contamination may be an unknown quantity that is greater than 100-percent more. This situation results when benzene has attenuated and poses no further risk, but significant concentrations of MTBE continue to migrate down-gradient and contaminate drinking water supplies. A graph of this distribution is presented in Exhibit 1.

Conclusion

Remediation of MTBE-contaminated soil generally does not pose an additional concern when a petroleum release has occurred because MTBE can often be removed from soil with-

out additional time or expense. But remediating MTBE-contaminated groundwater can be problematic. MTBE's high solubility in water, low rate of adsorption to soil, and low rate of biodegradation can make treating groundwater contaminated with MTBE more expensive than treating groundwater contaminated with petroleum that does not contain MTBE. Fortunately, there are proven treatment technologies available. Pump-and-treat is usually the most cost effective method, but in some cases air sparging may be appropriate. Other existing technologies may also prove effective as more case studies are reported. The potential for *in situ* biodegradation of MTBE is widely believed to be low, but new research may clarify our understanding of conditions that may make it an effective option. In addition to remediation of the source area, point-of-use treatment appears to be a common approach to addressing MTBE when contamination is limited to individual homes or private wells.

Exhibit 1. Preliminary Estimate Of The Incremental Cost Increase of MTBE Remediation in Groundwater At LUST Sites

