

API SOIL & GROUNDWATER RESEARCH BULLETIN

*A summary of research
results from API's Soil/
Groundwater Technical
Task Force.*

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TEN FREQUENTLY ASKED QUESTIONS ABOUT MTBE IN WATER

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Methyl tertiary-butyl ether (MTBE) is the most commonly used fuel oxygenate. MTBE is more soluble in water than benzene, toluene, ethylbenzene, and xylene (BTEX) and is less biodegradable than BTEX in the subsurface. There is also field evidence of MTBE occurring in groundwater at higher concentrations than BTEX. This bulletin is intended to assist those responsible for making assessment and remediation decisions at MTBE-impacted sites.

Question #1. Is MTBE a new gasoline compound?

MTBE was first blended in gasoline in 1979 to replace lead and to increase octane. Its use has increased rapidly over the last decade. In 1988 the first wintertime oxygenated fuel program was implemented in Denver using 15% MTBE (by volume) to reduce vehicle carbon monoxide emissions. Wintertime oxyfuel programs began in 30 other non-attainment areas in 1992-93. Reformulated gasoline (RFG) has 11% MTBE by volume and was introduced in ozone non-attainment areas in 1995. Other oxygenated compounds (for example, the alkyl ethers TAME, ETBE and DIPE, or alcohols like ethanol, methanol and TBA¹) have been used in gasolines (Zogorski *et al.*, 1997), and some have been in use as long as or longer than MTBE (Gibbs, 1990).

Question #2. Are MTBE's health effects known?

There have been extensive studies of the health impacts of MTBE on animals and humans. In a 1993 report, EPA established an inhalation reference concentration (RfC) for evaluating chronic noncancer health effects of 3 mg/m³ (EPA, 1993). Recent comprehensive reviews of MTBE's health effects have been conducted by the National Science and Technology Council and the Health Effects Institute. The National Research Council has also evaluated those studies. Melnick *et al.* (1997) provides a summary of all these recent reviews. A drinking water advisory for MTBE was released by EPA in December 1997 to provide consumer acceptability advice and information on health effects (EPA, 1997). It states that MTBE concentrations in the range of 20-40 ug/L (20-40 parts per billion) or less in water will likely avert unpleasant taste and odor effects, and that this concentration range is about 20,000 to 100,000 times lower than the range of exposure levels in which cancer or noncancer effects were observed in animal toxicology studies. Such EPA 'advisories' are issued for contaminants not subject to primary drinking water regulation. They are intended for guidance only, are not legally enforceable, and are subject to revision as new information becomes available.

Question #3. Can MTBE enhance BTEX solubility and transport?

Research has shown that cosolvency effects typically arise only when the cosolvent is present in water at 1% or more by volume (Zogorski *et al.*, 1997). Therefore, MTBE will not enhance the solubility of BTEX unless the concentration of MTBE in groundwater exceeds 10,000 mg/L (10,000 parts per million or 1%). This threshold concentration is much higher than frequently reported measurements at field sites, and exceeds the effective solubility of MTBE in water contacted by gasoline with 15% MTBE, shown in a lab study to be about 5,000 mg/L (API, 1991).

Question #4. Do MTBE plumes dive or sink?

MTBE has a specific gravity of 0.740, which is even less than the BTEX compounds. Therefore, as it is less dense than water it can not 'sink'. Dissolved constituents which are less dense than water can reach deeper groundwater in response to natural or induced hydraulic gradients and diffuse recharge. The most likely causes for the occurrence of MTBE in deep groundwater are steep vertical gradients caused by extraction wells which can pull dissolved constituents to greater depths, or cross contamination within or between aquifers due to poorly sealed wells.

Question #5. Can MTBE form narrow plumes?

All dissolved constituents can form narrow plumes if the groundwater flow direction remains constant over time. Aerobic biodegradation can limit the width of BTEX plumes due to the transverse diffusion of dissolved oxygen into the plume. Because biodegradation will be more significant for BTEX, the MTBE plume width should not be less than the BTEX plume width from the same gasoline release, it will likely be wider. However, a more recent release of MTBE at a site with an older BTEX plume may create a MTBE plume that is narrower than the older BTEX plume, or very small releases of MTBE may create small MTBE-only plumes due to complete biodegradation of the BTEX.

¹TAME = tertiary-amyl methyl ether

DIPE = diisopropyl ether

ETBE = ethyl tertiary-butyl ether

TBA = tertiary-butyl alcohol

Question #6. Do maximum MTBE concentrations exceed benzene concentrations at UST sites?

MTBE is much more soluble than benzene, is less biodegradable, and can be found in much higher concentrations in gasoline. Therefore, when detected in groundwater, MTBE concentrations typically exceed benzene concentrations found in the same sample. However, in spite of its greater solubility, very high concentrations of MTBE in groundwater do not appear to be common. One survey in California showed MTBE groundwater concentrations exceeding 10,000 ug/L at about 10% of the 245 sites examined (California EPA, 1997).

Question #7. If found in groundwater, is MTBE necessarily from a UST system?

Concentrations of MTBE in groundwater greater than about 30 ug/L originate from point sources (e.g., leaking UST systems), whereas lower concentrations may originate from both point sources and non-point sources (Zogorski *et al.*, 1997). Non-point sources include atmospheric washout (precipitation events in which MTBE partitions from the atmosphere) and stormwater that contains fuel residues from roads, parking lots, etc. (Pankow *et al.*, 1997; Delzer *et al.*, 1996). Groundwater impacted by these non-point sources is unlikely to exceed 2-20 ug/L

Question #8. Can MTBE be remediated in groundwater?

The presence of MTBE and other ether oxygenates in groundwater does not prevent the application of conventional active remedial methods such as air stripping, carbon adsorption, and soil vapor extraction (SVE) for gasoline spills but it may increase the cost (Zogorski *et al.*, 1997), depending on effluent discharge limits and remediation goals. *In situ* remediation technologies such as SVE, groundwater extraction, and air sparging are limited by the effectiveness of the remediation fluid (air, water) to contact all types of contaminants including BTEX, MTBE and other gasoline compounds.

Question #9. Is biodegradation a treatment alternative for MTBE in remediation effluents?

There are fewer published studies on the biodegradability of MTBE and other ether oxygenates than for petroleum hydrocarbons. Recently, a number of investigators (Salanitro *et al.*, 1994; Cowan and Park, 1996; Mo *et al.*, 1997; Steffan *et al.*, 1997), have isolated MTBE degrading cultures and organisms. API research has also demonstrated the effectiveness of bioreactors (API, 1997a). A MTBE degrading culture is being used to biodegrade MTBE contaminated groundwater in fluidized bed reactors (Mosteller *et al.*, 1997).

Question #10. How does MTBE affect the application of Risk-Based Corrective Action (RBCA)?

MTBE is included as a compound of interest in the ASTM 1995 RBCA standard, and that framework is appropriately applied to assessments of potential MTBE exposures. The fate and transport parameters for MTBE are understood sufficiently to use reasonably conservative modeling approaches to estimate its natural attenuation. However, only a few studies have attempted to characterize the *in situ* biodegradation of MTBE (Borden *et al.*, 1997; Schirmer and Barker, 1998; API, 1997b; API, 1998). While there is evidence that MTBE does biodegrade at some gasoline release sites, the existing biodegradation database is small at this time and might not be considered adequate to allow routine inclusion of a first order biodegradation rate constant without supporting site specific data. Accordingly, receptor point concentrations can be readily predicted

and MTBE can be included in the RBCA process. The noncarcinogenic reference concentration included in the ASTM RBCA standard and the EPA Drinking Water Advisory value of 20-40 ug/L may also be of use in estimating acceptable site cleanup levels.

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