

Oxygenates

A Circle Vicious

What Do We Know About the Other Oxygenates?

by Patricia Ellis

On January 18, 2000, then-Acting Director of EPA's Office of Underground Storage Tanks (OUST) Sammy Ng wrote to regional and state UST/LUST program managers urging them to "begin monitoring and reporting of MTBE and other oxygenates in groundwater at all UST release sites nationwide." He also recommended that if MTBE or other oxygenates are detected during monitoring activities, that states take "immediate and aggressive remedial action to address the contamination."

Ng went on to state that, while MTBE has received most of the publicity recently, it is by no means the only chemical of concern for which states should be monitoring and reporting. Tert-butyl alcohol (TBA) can be both a degradation product and a fuel additive in its own right. It is also potentially more toxic than MTBE. States were urged to consider assessing for other oxygenates, such as tert-amyl methyl ether (TAME), diisopropyl ether (DIPE), ethyl-tert-butyl ether (ETBE), ethanol, and methanol.

According to results of the NEIWPCC survey conducted in August 2000, most states were not assessing for the presence of fuel oxygenates, other than MTBE (42 states require sampling and analysis for MTBE in groundwater at LUST sites, and 29 require such sampling in soil). Maybe in the time since the NEIWPCC survey was completed, this picture has changed. Maybe the majority of states are now looking for all of the oxygenates, as OUST strongly urged. Right, and if you believe that, I've got a nice bridge to sell you. Kudos to the 4 or 5 states that are looking for most of the oxygenates most of the time.

I'd like to propose that we all start paying a bit more attention to the other oxygenates, because as you

will read, they may already be present at your friendly neighborhood LUST site. And, because I get this uncomfortable feeling that history is threatening to repeat itself.

A recent abstract by Andrew Gray and Anthony Brown for the National Ground Water Association Petroleum Conference in Anaheim, California neatly sums it up: "Many within the petroleum industry have suggested that it was overemphasis on benzene in the 1980s and early 1990s that caused them to neglect MTBE. It appears that we may not have learned from this oversight, and the pattern may be repeating itself. Where there is now an emphasis on MTBE, in many places they are not looking for or evaluating the potential impact from the other fuel oxygenates."

So let's take a glance at what we know or don't know about the other oxygenates within the contexts of health effects, risk-based corrective action (RBCA), natural attenuation, remediation and treatment, and analytical techniques. Since we do know a bit more about ethanol than TBA, ETBE, and TAME, I'll provide a brief synopsis on what we know about that substance.

Health Effects

According to a 1996 study by the Health Effects Institute, little or no information is available for ETBE, TAME, and DIPE; not enough information is available on the toxicity of ETBE and TAME to evaluate their potential health effects, but more research is being planned; no information is available on the toxicity of DIPE. The report recommended that a comprehensive set of studies be undertaken to determine levels of personal exposure to oxygenates using standardized protocols.

"Although more information on MTBE is needed," states the report,

"the need is particularly great for assessing exposure to ethanol, TBA, and TAME, because these compounds are currently in use (or may be soon) and the resulting exposures have not been adequately assessed."

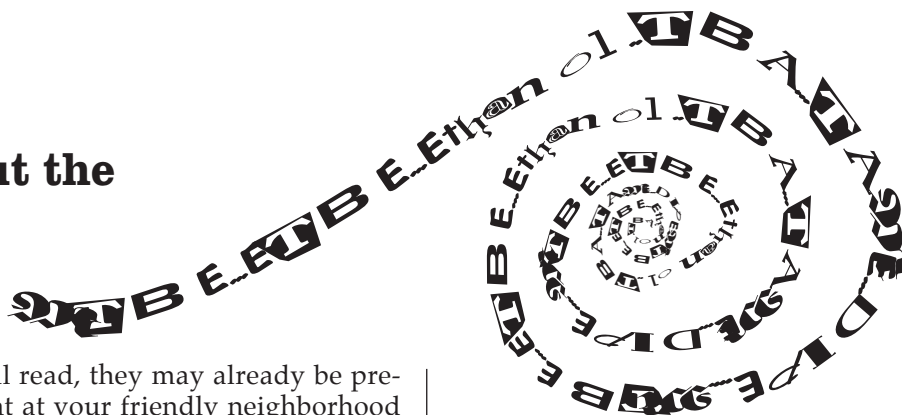
MTBE has been described as one of the most studied chemicals on earth, yet many studies have concluded that there is "not sufficient evidence" to declare it a human carcinogen even though animal studies show it to be a probable carcinogen. (Where will we be with some of the less-studied chemicals that occur in gasoline?)

Health effect studies are currently underway by industry and EPA to understand more fully the comparative risks associated with exposure to fuels both with and without oxygenates. Although the majority of the research is focused on inhalation-related health effects, the results should help us better understand the human health risks associated with exposure to fuels by any route.

TBA is a major metabolite of MTBE, regardless of the route of exposure. From a toxicological point of view, exposure to TBA elicits both noncancer and systemic toxic responses, as well as evidence of carcinogenicity. Animal testing of TBA in drinking water produced carcinogenic effects at high levels of exposure. Additionally, formaldehyde, also a metabolite of MTBE, is a respiratory irritant at high levels of human exposure and is currently considered by EPA to be a probable carcinogen (Class B1) by the inhalation route and, with less certainty, via ingestion (Blue Ribbon Panel Report, 1999).

Studies of groundwater from the City of Santa Monica's Charnock and Arcadia well fields in California

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revealed the presence of four non-MTBE fuel oxygenates—TBA, ETBE, TAME, and DIPE (Gray and Brown, 2000). The California Department of Health Services (CDHS) is particularly interested in TBA because of its increased mobility in groundwater and the difficulties in treating the chemical.

CDHS has established a Drinking Water Action Level of 12 µg/L for TBA. (Health-based advisory levels are established by CDHS for chemicals for which primary MCLs have not been adopted.) In September 1997, New Jersey issued an Interim Specific Groundwater Criterion of 100 µg/L for TBA. New Jersey lowered the concentration that it recommends as a goal for groundwater cleanups and for guidance in situations where groundwater is contaminated with TBA from 500 to 100 µg/L, based on the National Toxicology Program's TBA drinking water study on rats and mice (Linder, 2000).

RBCA

Regulatory policy has evolved in the last decade toward the increasing use of risk-based corrective action (RBCA) as a basis for making LUST site remediation decisions. The rise in RBCA-type programs paralleled and was assisted by an increased understanding of the role of natural attenuation and intrinsic bioremediation in limiting the migration of dissolved hydrocarbon plumes. Because of their chemical properties, modeling fate and transport of the oxygenates can be more difficult.

RBCA, however, focuses on health risks, and little information is available for most of the oxygenates. MTBE has been shown to present aesthetic (i.e., taste and odor) problems at relatively low levels, and alternative RBCA guidance may need to be developed to adequately address those types of environmental concerns. (See Table 1.)

Then again, how many state RBCA programs can take aesthetics into account, rather than strictly health? There are only a few states where secondary standards are enforceable for public water systems. Both TAME and ETBE have even

TABLE 1 TASTE AND ODOR THRESHOLDS FOR BENZENE AND OXYGENATES IN GASOLINE

	Benzene	MTBE	Ethanol	ETBE	TAME	TBA
Taste threshold in water (µg/L)	500	20-40	—	47	128	—
Odor threshold (ppm)	0.5	0.053	49	0.013	0.027	21

From Blue Ribbon Panel Report (1999).

lower odor thresholds than MTBE (but the taste thresholds for both are higher than for MTBE). At least you may be able to smell them sooner.

In contrast, TBA does not have a low taste or odor threshold, so it is possible to be exposed to high levels without noticing it. Likewise benzene—you can be exposed to unhealthy levels in drinking water without being able to smell or taste it. Thus the two chemicals that are **unhealthier** for you are the ones that you can be exposed to more easily without realizing it.

Both New Hampshire and California have secondary drinking water standards that are lower than the primary standard for MTBE. Do we need to do the same thing with ETBE and TAME?

Natural Attenuation

RBCA programs have been able to take advantage of the fact that the BTEX components of gasoline tend to naturally attenuate with time and with distance from a source area. MTBE and the other ether oxygenates (probably to a lesser degree) are thought to be more recalcitrant to biodegradation in the environment.

A recent BP/Amoco study (Kolhatkar, Wilson, and Dunlap, 2000) looked at 74 sites in Pennsylvania, New Jersey, New York, Florida, Indiana, Maryland, and Washington, DC to determine whether natural biodegradation of MTBE under anaerobic subsurface conditions at some sites may control migration of MTBE and TBA plumes. (TBA is a known intermediate of MTBE biodegradation, it is present in some gasoline-grade MTBE, and it was also used as a gasoline blending component circa 1975-85.)

Groundwater samples were collected and analyzed for VOCs (MTBE, TBA, alkylbenzenes, including benzene, toluene, ethylbenzene, and the xylene isomers, and three

trimethylbenzenes) and a suite of geological parameters, including dissolved oxygen, dissolved methane, ferrous iron, total organic carbon, sulfate, nitrate, alkalinity, and pH. First order biodegradation rate constants were estimated for MTBE, TBA, and benzene at a number of the sites.

Data suggest that natural biodegradation of MTBE and TBA under anaerobic conditions at some sites may control migration of MTBE and TBA plumes. There appeared to be a good correlation between strongly anaerobic plume geochemistry and natural MTBE biodegradation in the subsurface in the methanogenic area of the plume caused by BTEX degradation. Unfortunately, because the study was designed to address the biodegradation of MTBE (along with TBA), other oxygenates were not included in the list of analytes.

In the study, biodegradation rate constants for MTBE, TBA, and benzene were estimated using the approach of Buscheck and Alcantar (1995). Natural biodegradation could be demonstrated at only four of the 74 sites, because the statistical method required the existence of at least five monitoring wells along the centerline of the plume. Three of the sites (where there was statistical evidence for degradation) were where the geochemical environment was methanogenic and sulfate depleted; one site was weakly methanogenic with available sulfate. An additional 44 other sites fell into those geochemical categories and thus were thought by the authors to also have environments conducive to biodegradation.

The authors believe that natural MTBE biodegradation was occurring at many of these sites, but it could not be demonstrated by the statistical methods used in this study. Rates of anaerobic biodegradation of MTBE and TBA were comparable to benzene.

At the sites, the concentrations and frequency of TBA occurrence in groundwater were comparable to those for MTBE. There was little difference in the relative concentrations of TBA and MTBE in groundwater between the sites where MTBE biodegradation was apparent and sites where it was not. The relative concentrations of TBA and MTBE alone may not be a reliable indicator of in-situ biodegradation potential.

TBA was detected in groundwater samples from all six states and DC. The highest TBA concentration was 223,000 µg/L; 10 samples exceeded 50,000 µg/L; and 29 samples were in the 10,000-50,000 µg/L range. The MTBE:TBA ratio was nearly 1:1. With numbers as high as these, it seems fairly obvious to me that we should always be looking for TBA in our groundwater samples, even when we aren't trying to determine whether MTBE is degrading to TBA.

It is doubtful that many of these sites have been investigated thoroughly in a three-dimensional manner. The statistical method used required that there be at least five monitoring wells located along the centerline of the plume. No mention was made as to whether any of the sites had been characterized using any form of multilevel groundwater sampling that would detect whether any of the plumes were "diving."

A similar problem exists with both the California, Texas, and Florida MTBE plume studies (Happel, Beckenbach, and Halden, 1998; Mace, 1998; and Integrated Science and Technology, 1999). Plume lengths were determined (to a specific concentration of MTBE) based on monitoring well data. Monitoring wells for these sites were likely screened in the traditional manner for gasoline sites, at the top of the water table. It is unlikely that monitoring included multilevel sampling designed to detect a "diving" plume, therefore plume lengths measured may not represent the "true" plume lengths for the sites. What effects would this additional information have on the findings of the natural attenuation study?

A recent study by Kramer and Douthit (2000) was performed to determine whether the presence and widespread occurrence of TBA in groundwater could be explained as a

degradation product of MTBE, or whether TBA was originally present in significant quantities in gasoline as an impurity or as an oxygenate. Literature reports (e.g., Salanitro, 2000) indicate that natural MTBE biodegradation is a relatively slow process.

The study involved mixing experiments in the laboratory, where gasoline samples from five New Jersey gasoline stations were mixed with water to determine the types and concentrations of oxygenates detectable. The solubility of each of the oxygenates is related to the pure compound solubility in water and the mole fraction of the oxygenate in the mixture.

All gasoline/water mixture samples showed TBA in the water phase at approximately 83% of the dissolved MTBE concentration. The average MTBE concentration in the water samples was 1,638,000 µg/L, and the average TBA concentration was 1,356,000 µg/L. In addition, all samples contained methanol in concentrations ranging from 26,000 to 51,000 µg/L. One sample contained 17,300 µg/L ethanol, and the average TAME concentration was 4,370 µg/L (one sample contained 153,000 µg/L TAME). DIPE, ETBE, and TBA were not detected in any of the five samples. Total BTEX concentrations were about 0.75% of the total oxygenate concentration.

Kramer and Douthit caution that the wide occurrence of TBA at similar concentrations to MTBE indicates that care needs to be taken in drawing conclusions about potential biological decay under field conditions using TBA as an indicator. There are significant differences in the solubility of MTBE and TBA. The solubility of pure MTBE in water is approximately 48,000 µg/L; the solubility of

MTBE at 11% by volume in gasoline is approximately 5,000 ppm, while TBA is totally miscible in water. A relatively small percentage of TBA in MTBE could result in a significant concentration in the water-soluble phase.

Treatment/Remediation Systems

Before you can remediate groundwater contamination, you need to fully delineate the plume—area, analytes present, concentrations, and variations with depth. Characterization of a site includes both vertical and horizontal delineation. Because of the tendency of MTBE to move deeper into the aquifer in some environmental settings, you must also focus on identifying its three-dimensional characteristics, searching vertically for its presence through direct-push sampling, clustered short-screen monitoring wells, and the like.

When you think you are at the end of your plume, you should look deeper, to make sure that it isn't sneaking below the bottom of your well screen. Too often, I fear, we set about characterizing our LUST sites wearing blinders, hoping not to discover too much.

After all, ignorance is Bliss! Harmful by-products created during one of the oxidation processes? Not to worry. Didn't even know about the possibility! And let's face it, the more we find, the greater the cleanup cost.

Table 2 summarizes some groundwater monitoring data from one of my LUST sites in Delaware. The three sampling locations are along the centerline of the plume. Several months prior to these analy-

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TABLE 2 GROUNDWATER MONITORING DATA FROM A LUST SITE IN DELAWARE
(Concentrations in µg/L)

Contaminant	Tank Field	30 Feet Downgradient	100 Feet Downgradient
Benzene	330	1,150	<5
Toluene	472	6,070	<5
Ethylbenzene	1,870	1,950	<5
Xylenes	2,720	14,600	11
MTBE	46,100	3,120	650
TAME	10,900	51,500	31
TBA	29,500	782	2,420

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ses, the MTBE concentration in the tank field was 310,000 $\mu\text{g/L}$.

The consultant for the project considered using an advanced oxidation technology (AOT) for ground-water treatment. Based on predicted flow rates and contaminant concentrations, the vendor provided equipment cost estimates for a UV/peroxide system (\$167,000 for equipment and \$5.00/1,000 gallons treated) and for a UV/Ozone system (\$375,000 for equipment and \$2.32/1,000 gallons treated). The vendor indicated that BTEX and MTBE could be treated to less than 5 $\mu\text{g/L}$, but that TBA and TAME effluent values were "to be determined."

According to the vendor, the oxidation of MTBE will form a series of intermediates—acetone, acetic acid, t-butyl formate and t-butyl alcohol are the most predominant. A portion of these intermediates are oxidized in the AOT process. Residual intermediates are readily biodegradable. A biological oxidation system can be attached to the treatment train if necessary to meet permit requirements. Discharge limits for the various oxygenates present must be determined.

Blah, blah, blah. I think I'd be happier only knowing about the BTEX and MTBE (and I still don't know whether ETBE, DIPE, or ethanol might be present at this site). My point is that it is certainly frustrating and costly to deal with yet another contaminant of concern.

In pilot tests conducted at Santa Monica's Charnock well field (Linder, 2000), using Calgon's UV-peroxide technology, samples spiked with 1,000 $\mu\text{g/L}$ MTBE and 400 $\mu\text{g/L}$ TBA required 40% more energy to treat than water spiked with 1,000 $\mu\text{g/L}$ MTBE alone. I don't know whether the cost estimates for my site took into account these potentially higher costs for destruction of several different oxygenates.

Analytical Techniques

Unfortunately, EPA's memorandum recommending monitoring and reporting of MTBE and related oxygenates in groundwater for LUST

sites comes without specific guidance on measurement techniques to be employed. EPA Method SW-846, applicable to LUST sites, does not contain a validated protocol for MTBE analysis.

Although this lack of protocol may change in the future, an approved or required method is still unlikely because EPA's waste program favors a performance-based approach that leaves the choice of methodology to project managers and analytical chemists. Accordingly, monitoring of fuel oxygenates may be performed by any method suitable for accurately measuring the constituents of concern in the matrix of concern at the action level of concern.



Too often, I fear, we set about characterizing our LUST sites wearing blinders, hoping not to discover too much. After all, ignorance is Bliss!

Halden and others (2001) recently published an evaluation of the standard methods for the analysis of MTBE and other fuel oxygenates in gasoline-contaminated groundwater. Consistently good results were obtained with EPA Method 8240B/60B (mass spectrometry) and ASTM Method D4815 (flame ionization detection). EPA Method 8020A/21B (photoionization detection) was unfit for monitoring of TBA and frequently yielded false-positive and inaccurate results when ether oxygenates were monitored in aqueous samples containing high concentrations of TPH (>1,000 $\mu\text{g/L}$).

If we're going to get out and analyze, let's get good data! Numerous state studies have been now been

completed to identify the extent of the MTBE problem and yes, it is a big problem. MTBE has been added as an analyte at LUST sites in most states, and larger public water systems must now monitor for it as an unregulated contaminant.

The Maryland Department of the Environment (MDE, 2000) recently finished compiling information on the occurrence of MTBE in community water systems and has compiled a database of impacted domestic wells. The Maryland MTBE Task Force has recommended that MDE continue its effort in the coming year to determine the extent of MTBE and TBA contamination. Now states need to determine whether similar problems exist with any of the other oxygenates.

What About Ethanol?

We are on somewhat firmer ground with respect to predicting how ethanol should behave in the environment and how certain remedial technologies are expected to perform. Ethanol is infinitely soluble in water, and its low K_{ow} (octanol-water partition coefficient) indicates that it has a very strong affinity for dissolution into water. These data suggest that ethanol in residual phase will be leached out more readily than other compounds and can potentially reach higher aqueous concentrations.

Cosolvency effects of ethanol with benzene (and other hydrocarbons) may be an issue, particularly if neat ethanol is spilled in an area where there has been a hydrocarbon spill, such as at a terminal where neat ethanol is blended with gasoline prior to distribution to retail gasoline facilities (Powers, Rice, Dooher, and Alvarez, 2001).

The vapor pressure of ethanol is moderately high from free-phase gasoline, indicating that soil vapor extraction, air sparging, and air stripping could be effective in removing ethanol from pure product. However, ethanol has an extremely low volatility from dissolved-phase to vapor-phase, as indicated by its low Henry's law constant; therefore, once dissolved into groundwater, ethanol is unlikely to volatilize significantly under ambient conditions and can also be difficult to remove from water by air stripping.

Sorption characteristics influence the movement of a compound in groundwater and the effectiveness of water treatment using carbon adsorption. The low organic carbon partition coefficient (K_{oc}) for ethanol indicates that it will sorb poorly to organic carbon, therefore ethanol is not expected to be significantly retarded as groundwater moves downgradient, and carbon is not expected to perform well as a treatment technology.

Ethanol appears to biodegrade readily under most aerobic and anaerobic conditions. However, because it is preferentially consumed by microbes, the biodegradation of BTEX compounds may be inhibited.

Although ethanol's chemical properties are well known, and it should be possible to predict its fate and transport properties and response to various treatment technologies, there is a general lack of ethanol monitoring data in the literature.

Ethanol groundwater monitoring is scarce, at least in part, because most regulatory agencies do not require ethanol analysis. Furthermore, it appears that no state agencies have as yet set concentration limits for ethanol in groundwater or drinking water.

Creek and Davidson (2000) could not locate any ethanol remediation sites. The extent of any current possible problem and cost associated with cleanup are unknown.

The Blue Ribbon Panel recommended the lifting of the oxygenate mandate that forces the use of an oxygenate in gasoline. Unfortunately, politics, rather than sound science, will probably be the driver as to whether ethanol will take the place of MTBE, or whether refineries will be permitted to blend oxygenate-free gasoline.

Is There a Lesson Here Somewhere?

A recent article by Franklin and others (2000) reminds us of some of the ways that got us where we are today—faced with a national MTBE problem. They point out that policy makers only belatedly realized the environmental ramifications of increased levels of MTBE in gasoline. The policy process that led to MTBE's

predominance was flawed, since no systematic attempt was made up front to evaluate all possible implications of MTBE's widespread use.

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The history of MTBE in the United States illustrates several typical, but problematic, features of environmental policy making. It reveals how the scale of chemical usage directly impacts environmental effects. It highlights how institutional factors constrain policy makers through statutory mandates, regulatory agency organizational structures, and the strong influence exerted by politics and economics even in supposedly "technical" debates.

Finally, the MTBE case reveals barriers to effective scientific and technical communications among policy makers, regulated industries, special-interest groups, and the public. Will we just be substituting another chemical name for MTBE?

An article by Erdal and Goldstein (2000) discusses lessons for environmental policy that we should have learned as a result of choosing MTBE as a gasoline oxygenate. They identified 14 government initiatives during the 10-year period from 1989 to 1999 in which the potential adverse consequences of MTBE were considered, and a nearly identical research agenda was proposed. More research is needed, not further reviews of research already completed.

What are some of the lessons that should have been learned from MTBE?

- Research should precede rather than follow environmental health policy decisions.
- The extent of potential human and environmental exposure should be an important criterion in determining the amount of information needed before making an environmental policy decision.

- The boundaries between various EPA program offices should be as fluid as the boundaries between the environmental media. Air, water, and waste programs should all be working hand-in-hand.
- It is more difficult to remove a chemical once it is in commerce than it is to prevent its use. (The Bush administration requested that EPA's proposal to ban MTBE under TSCA be withdrawn, at least at the present time.)
- Replacing MTBE with other, less well-studied oxygenates, such as TAME or ethanol, is poor environmental policy.

Those who remember the MTBE story on CBS "60 Minutes" in January 2000 may remember this exchange between EPA's Bob Perciasepe and CBS:

CBS: Have there been studies done on the health effects of MTBE in the drinking water?

Perciasepe: Not enough. Not enough.

CBS: But any? I mean, have any been done?

Perciasepe: "I'm not aware of any specific studies that have been done on that."

CBS: "What are you doing about the problem? Right now. I mean, what has been done since this first memo in 1987? What's been done?"

Perciasepe: "Not enough."

Will some future EPA official be answering questions about the other oxygenates the same way in a few years? EPA's Blue Ribbon Panel Report summarized impacts of MTBE to ground and surface water resources in the U.S. It also stated that the body of information available to evaluate impacts of other gasoline oxygenates on water resources is significantly more limited. It's time to start looking at the extent of the problem. ■

[NOTE: References for this article can be found on page 23.]

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