MTBE as a Ground Water Contaminant

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Abstract

MTBE (Methyl tertiary Butyl Ether) is now among the top fifty chemicals produced in the United States. It is used exclusively as an octane enhancer in gasoline, in which it constitutes up to 11 percent of total volume.

MTBE is soluble in water at 4.3%. This compares with the relative insolubility of benzene (0.18%), toluene (0.05%), and xylene (0.02%). However, the BTX compounds are more soluble in MTBE than they are in water. When gasoline plus MTBE leaks to ground water, the MTBE spreads both further and faster than the gasoline, and the concentration of gasoline dissolved in ground water increases.

We have investigated several cases of ground water contamination resulting from spills of gasoline with MTBE. In one such case, several household wells became contaminated with MTBE only. In one household, concentrations of up to 690 ppb MTBE were measured, (with other gasoline constituents combined at less than 10ppb). The well nearest the spill had concentrations of up to 126,000 ppb gasoline including MTBE. At another site, concentrations exceeded 600,000 ppb gasoline including MTBE. This contrasts with the usual maximum dissolved concentration of gasoline in ground water near spill sites of about 10-30,000 ppb (when no MTBE is present).

Toxicity data on MTBE indicate that it is an irritant like many of the other components of gasoline. Maine has set a maximum contaminant level of 50ppb.

Ground water contaminated with MTBE is difficult to remediate. Filtration through activated carbon is not cost effective for MTBE: a 2 cubic foot bed lasts a month or less as a household treatment system, even with an influent concentration of MTBE as low as a few parts per billion. However, air stripping systems are capable of removing MTBE, but only if very high air to water ratios are used.
Introduction

With the reduction in lead content of gasolines, octane enhancement is now achieved by several compounds, including ethanol, methanol, tertiary-butyl alcohol (TBA), Oxinol™ (a blend of methanol and TBA), "reformate", "alkylate", or extra doses of toluene and xylene. But the additive which is increasingly popular at the refineries where gasoline is blended is MTBE (methyl tertiary-butyl ether, also known as TBME, or sometimes as 2-methoxy 2-methyl propane), the subject of this paper.

Facts about MTBE

MTBE is an "oxygenate" and one of the few compounds in gasoline to contain oxygen. Its structure is given in Fig. 1.

\[
\begin{align*}
\text{CH}_3 & \\
\text{CH}_3 & -\text{O} & - & \text{C} - & - & \text{CH}_3 \\
\text{CH}_3 &
\end{align*}
\]

Fig. 1. Chemical structure of MTBE. The horizontal CH\textsubscript{3}-O-C bonding represents the ether molecule, while the vertical CH\textsubscript{3}-C-CH\textsubscript{3} unit represents a propane molecule.

MTBE is now among the top 50 chemicals produced in the United States (47th by weight in 1984, 44th in 1985: Chemical and Engineering News, June 1985 and 1986). ARCO and Texas Petrochemicals are the major producers of MTBE, most of which is made for sale to other refineries where it is blended into gasoline. 30 plants now produce MTBE throughout the world, with an additional 20 planned. Total U.S. production is now running over 10,000 barrels per day (Octane Week, Feb. 2, 1987). Currently, 95% of that total is produced in Texas, from where it is shipped, either pure or blended in gasoline, to other parts of the US east of the Rockies. At present, little is used in western States, in Canada, or in Europe. However, MTBE use in the west and in other countries is expected to increase with increasing emphasis on lead phasedown.

MTBE was first produced by ARCO in the 1960s, when they patented a process for removing branched olefins such as isobutylene from hydrocarbon streams. MTBE is manufactured by reacting this isobutylene with a small amount of methanol. It was not until 1979, however, that MTBE was first produced commercially. Since 1980, production has increased at a rate of about 40% per year. It is currently used in about 10% of the nation's gasoline, though the proportion of gasolines with MTBE may be much higher in some parts of the US. (From ARCO advertising materials and personal communications.)
EPA allows the blending of MTBE into gasoline up to about 11% by volume. The exact proportions of MTBE in a particular gasoline depend on the composition of the crude, the octane rating of the distillate, and the required octane rating of the final blend. MTBE is usually blended at between 2 and 7%. MTBE is used in both unleaded and "regular" gasolines. Usually the highest proportions are to be found in unleaded premium. (ARCO, personal communication.)

Among other claims made about MTBE are: 1) it has a blending octane value greater than that of toluene, reformate or alkylate; 2) it is compatible with all types of automotive and tank liner materials; 3) it does not have a phase-separation problem in the presence of water (which is a problem with ethanol and methanol); and 4) its use in gasoline reduces carbon monoxide and hydrocarbon emissions in most cars (from ARCO's advertising pamphlets).

Transport and Fate of MTBE in the Environment

MTBE is soluble in water at 4.3% (ARCO data). This compares to the relative insolubility of other major components of gasoline, as summarized in Table 1.

<table>
<thead>
<tr>
<th>Component</th>
<th>Equilibrium Solubility in Water (mg/l)</th>
<th>Relative to Benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1780</td>
<td>1.0</td>
</tr>
<tr>
<td>Toluene</td>
<td>515</td>
<td>0.3</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>170</td>
<td>0.1</td>
</tr>
<tr>
<td>MTBE</td>
<td>43,000</td>
<td>24.0</td>
</tr>
</tbody>
</table>

(Data from API, 1983, Table 2-1 for BTX. That source gives a range of values for each component. Data for MTBE from ARCO factsheets.)

Though it is important to realize that the equilibrium solubilities listed above are rarely reached in nature, the significance of the figures lies in their ability to predict how MTBE behaves as a ground water contaminant relative to other components of gasoline, of which benzene is the most soluble (API, 1983, table 2-2).

MTBE is only used as an additive of gasoline. Thus one can assume that, except perhaps around refineries, the presence of MTBE in ground water signifies the nearby presence of gasoline.

When gasoline leaks to ground water, it contaminates the unsaturated zone and the water table with free product in the vicinity of the leak. Recharge to ground water by precipitation percolates through this product contamination zone, dissolving components of gasoline in approximate proportion to their solubilities. Although we know of no laboratory data, we infer that the concentration of MTBE in the recharge water will be considerably enhanced over that of the other components of gasoline for the following two reasons:

First, MTBE is at least an order of magnitude more soluble than other components of gasoline. Second, at a concentration of up to 11% of the pure product, MTBE may be one of the largest components of the spilled gasoline.
Once in the zone of saturation, the dissolved components travel with ground water. Concentrations of contaminants diminish as distance from the spill increases because of dilution, sorption onto soil particles, and biodegradation (Barker, Patrick and Major, 1987). In general, sorption of organic compounds is inversely proportional to their solubility (API 1985, p.4), so we expect MTBE to have a low sorption onto soil particles.

From the above, we infer that a plume of MTBE in ground water should be more extensive than the plume of other gasoline components. There should be areas on the outer fringes of the total plume where MTBE is the only detectable contaminant. The MTBE plume will appear as a "halo" around the dissolved gasoline plume, which in turn appears as a halo around the free product plume.

The greater solubility of MTBE in water, combined with the near 100% solubility of all gasoline components in MTBE may increase the sum total of all dissolved gasoline components in ground water. If this is so, then spills which contain MTBE should result in higher concentrations of total dissolved hydrocarbons in ground water than spills with no MTBE. This would have a co-solvent effect in the sense of Munz and Roberts (1986).

With respect to the biodegradability of MTBE, Fujiwara and others (1984) found that the presence of MTBE had little effect on the biodegradability of blended gasoline. But they did not discuss the biodegradability of MTBE alone.

Identification and Quantification of MTBE in Ground Water

The first indication of the presence of MTBE in domestic water supplies comes from its odor. It is said to have a "terpene-like" odor (ARCO personal communication), but householder more often describe it simply as a "chemical" odor. Our first contamination case, in 1984, was initially mistaken for one of hazardous waste leachate because of the unusual smell. From a large number of cases of contaminated domestic wells we have found that people can detect the odor of MTBE in their water at concentrations as low as 20-50 parts per billion.

In the lab, the identification of MTBE is difficult when it is associated with the other components of gasoline (e.g. Fig. 2a), but is simple when it occurs as a single component in water (Fig. 2b). At the Public Health and Department of Environmental Protection Laboratories in Maine, gasoline is analyzed in water using head space gas chromatography (GC). Fig. 2a shows the kind of scan which that method produces. Each constituent of the mixture shows itself as one or a series of peaks, but the peaks themselves do not provide unique identification because their exact position on the scan can vary depending on chromatographic conditions.

Because gasoline is initially a variable mixture, with each component having its own unique solubility and sorptive properties, every different spill has a different GC trace. We have found, however, that MTBE separates out as a distinct peak between the usually prominent peaks of iso-pentane and 2-methyl-pentane. The exact time of its emergence on the GC scan is dependent on column length, whether packed or capillary columns are used, and the specific temperature program of the run.

(Note that this is not a standard EPA method, though it is most akin to Method 601. Our State labs in Maine do not separately identify benzene, toluene, xylene and ethylbenzene as the indicators of gasoline contamination, because we believe that the many other components should not be ignored. If your laboratory chemists only identify the BTX components, then they should obtain an MTBE standard and separately identify it along with BTX. If your lab follows a total hydrocarbon analytical method, like Maine's, it is still useful to get the lab to separately identify and quantify MTBE. This is because gasoline with MTBE behaves differently in ground water than gasoline alone. For further details on laboratory procedure, contact the Jack Krueger at the Public Health Lab, State House Station # 11, Augusta, ME 04333, (207) 289-2727.)
Fig. 2a, (left). Gas chromatographic trace of a gasoline standard (without MTBE) diluted to 100 parts per billion. Notice that there are many peaks, none of which can be separately identified without mass spectrometry. The prominent peaks at 5.75, 10.50 and 16.69 minutes emergence represent iso-pentane, 2-methyl-pentane and toluene respectively.

2b, (right). GC trace of household well water with MTBE as the only detectable contaminant, with a peak at 8.34 minutes. It was quantified at 106 ug/l (ppb). The smaller peaks to the right are attributed to “column bleed”.

If MTBE is suspected in the sample, the particular GC peak can be analysed by mass spectrometry (GC/MS) as it comes through the column. An example of the resultant peaks is given in Fig. 3. Such analysis provides a choice of a small number of compounds most likely to produce the peaks. The chemist then has to do some detective work to pick the compound most likely to be present given the chemical context. Support for the choice comes from a library of standards of mass spectrometric patterns.

The head space GC and GC/MS techniques are not optimized for the detection and quantification of MTBE, so the detection limit is in the range of 5 ppb for GC and 100 ppb for GC/MS. The problem is that MTBE, with its high water solubility and low vapor pressure, only slightly partitions into the gas phase of a headspace vial at 70°C. To lower the detection limit, a purge and trap technique can be used to further concentrate MTBE prior to analysis by GC, or the sample can be directly injected into the column.
Fig. 3. GC/MS analysis of an MTBE standard provided by ARCO.

a) Total ion chromatogram: MTBE should show as a single peak — the small multiple peaks to the left are impurities, and the large multiple peak may indicate that the machine was "peaked out".

b) Mass spectrum. MTBE actually has a molecular weight of 88, but because it loses one methyl group (atomic mass of 15) during the GC/MS procedure, the major peak is at a mass of 73. There are also characteristic minor peaks at and surrounding 43 and 57. The tiny peaks to the right are interpreted as background noise.

Quantification of MTBE and gasoline in water is another problem. MTBE alone is relatively simple to quantify, because the height of its GC peak can be compared with that of a known concentration of standard MTBE. But for gasoline, the mixture of components in the original spill is usually not known, and in any case the composition of the mixture changes as it filters through the soil and aquifer. To further complicate matters, the components of gasoline all have different GC responses, (i.e., component A at a concentration of 20 ppb may produce a peak as large as component B at 50 ppb). So the quantification of gasoline in water can only be considered a crude approximation, one that is based on a comparison of the area under the total curve of all peaks, as compared to a similar curve obtained for what is likely to be a somewhat different gasoline standard.
The unhappy result is that the estimated concentrations of MTBE and gasoline in a sample are not really comparable, except as apples and oranges. In the future we will be concentrating on eliminating this source of confusion in analytical results.

Case Studies of MTBE/Gasoline Plumes in Maine

Our first case in Maine was in a rural part of North Berwick in the southwestern part of the state. The case was discovered in mid-1984, and for several reasons is thought to have been a recent spill. A farmer's tank was found to have been leaking product directly into the fractured schistose bedrock. Due to the configuration of the bedrock surface, the product plume was located on the other side of the road, about 150 feet away from the tank (Fig. 4). Product recovered from the pump hose and from the product plume was chromatographically identical, and found to be a leaded gasoline containing about 3% MTBE by volume.

The first household to receive contaminated water was the farmer's neighbor across the road, whose 80 ft deep drilled well rather suddenly produced water contaminated with 126,000 parts per billion total gasoline including MTBE. Because the spill occurred near the crest of a ridge, the dissolved plume spread in two directions downslope. Within months other homeowners only a few hundred yards from the spill site were complaining of water smelling hot of gasoline, but of "a funny chemical smell". Two years later and with the plume either stable or enlarging only slowly, most of the plume was an MTBE only plume occurring as a halo around the dissolved gasoline plume (Fig. 4). Water from some wells has been analysed as containing as much as 690 parts per billion MTBE with no detectable gasoline. Table 2 summarizes analyses from a recent sampling run of the monitoring wells on the north side of the hill.

Table 2: Analyses of MTBE and Gasoline from wells at the Cabbage Hill site in North Berwick, Maine (July, 1986).

<table>
<thead>
<tr>
<th>Well #</th>
<th>Location (see Fig. 4)</th>
<th>Gasoline (ppb)</th>
<th>MTBE* (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>Plume &quot;hot spot&quot;, at water table</td>
<td>304,069</td>
<td>236,250</td>
</tr>
<tr>
<td>1d</td>
<td>same, at 60ft depth</td>
<td>4,383</td>
<td>8,941</td>
</tr>
<tr>
<td>3</td>
<td>edge of product plume</td>
<td>48,543</td>
<td>46,800</td>
</tr>
<tr>
<td>2</td>
<td>200 feet downgradient</td>
<td>6,484</td>
<td>7,534</td>
</tr>
<tr>
<td>5</td>
<td>600 feet downgradient</td>
<td>nd</td>
<td>219</td>
</tr>
<tr>
<td>4</td>
<td>also 600 feet downgradient</td>
<td>nd</td>
<td>593</td>
</tr>
<tr>
<td>6</td>
<td>750 feet downgradient</td>
<td>nd</td>
<td>197</td>
</tr>
</tbody>
</table>

* note that quantification of gasoline and MTBE can only be compared like apples and oranges (see previous section). However, it should also be noted that the chromatograms for samples from wells 1-3 show large concentrations of the many other components of gasoline, much larger than is logically deduced by subtracting the MTBE concentration from the gasoline concentration.
Fig. 4. Map of the spill and plumes of gasoline and MTBE at North Berwick, Maine, showing contaminated wells, monitoring wells, and the suspected maximum limits of the three plumes. Numbers next to monitoring wells are same as numbered wells of Table 2. The aquifer beneath the entire hill is schistose bedrock with dominant fractures trending NE-SW. Natural sinks for the plume are the pond to the north, and an intermittent stream emanating from the spring to the south.
We have so far identified about 30 other sites in Maine where MTBE is a component of the spilled gasoline. This accounts for about 90% of the recent analyses which we have routed through the Public Health Lab. They all seem to follow the same general pattern that:

1) concentrations of gasoline and MTBE in ground water at the center of the plume can be extremely high. Our record high concentration so far is over 600,000 parts per billion in one household well with the intake pipe beneath floating product in a sand and gravel aquifer. This contrasts with the usual maximum concentration for similar situations without MTBE of about 10-30,000 parts per billion.

2) MTBE can occur as the only contaminant above detection limit over large areas of the plume. In one plume, believed to have originated from a small driveway spill, MTBE was the only detected contaminant of the spill.

3) the MTBE plume seems to occur as a halo around the gasoline-plus-MTBE plume. Where the plume is expanding, detection of MTBE precedes detection of gasoline in contaminated wells.

Toxicity of MTBE

The American Petroleum Institute, and several MTBE producers have run a battery of toxicity tests to assess its hazards. A summary of the results of these tests is as follows:

Within the limits of the testing, MTBE was found to be not very toxic, with effects similar to those which are characteristic of other ether compounds such as diethyl ether, formerly the standard surgical anaesthetic. It appears not to be genotoxic, and because it was "negative with and without activation" on the Ames test, it is probably not carcinogenic. MTBE is, however, a skin and eye irritant in more than one rodent species at high doses.

ARCO's health monitoring of their workers at MTBE manufacturing and transport facilities seem to indicate no adverse effects at time weighted average doses of up to 3ppm in air. But as is commonplace with any ground water contaminant getting into household water supplies, the concern it raises and the aggravation it causes the affected householders is a serious health effect independent of its toxicity.

Four reasons for concern over the toxicity of MTBE, and its presence in domestic well water are the following:

1) It is very mobile in ground water. Thus concentrations recorded from a well one week may be quite different the following week. Occasionally we have noted increases in the concentration of MTBE in domestic supplies of about an order of magnitude within a couple of days. Thus it is important to reduce concentrations in domestic water supplies as soon as they are discovered.

2) Plumes of MTBE in ground water are associated with plumes of gasoline, with its more varied and toxic components. Thus detection of MTBE should be considered a warning bell.

3) There is concern over MTBE's irritant properties.

4) MTBE is probably a nervous system depressant (like other ethers and the BTX components of gasoline) at high concentrations.

With these considerations in mind, the State Toxicologist for Maine has set a recommended maximum concentration level for MTBE in domestic water at 50 parts per billion, the same as for gasoline.
Removal of MTBE from Household Ground Water Supplies

Treating ground water supplies contaminated with MTBE is considerably more difficult than when gasoline alone is present.

Typically, granular activated carbon (GAC) is used as an interim measure to remove gasoline contamination from household ground water supplies (Hall and Mumford, 1987). But MTBE, with its relatively high solubility, is poorly adsorbed by GAC; thus breakthrough of MTBE comes early. Laboratory (API, 1983; and Lowry, unpublished experiments) and field (DEP experience) data substantiate this point. In general the bed life of GAC units is less than 25% of what it would be if no MTBE were present. Or, in practical terms, a typical 2 cubic foot GAC unit will last only a few weeks or months when MTBE is present (the length of time being dependent on concentrations of contaminants, rate of water use, and the brand and type of GAC employed). Because the cost of GAC treatment is primarily in the replacement of the carbon bed, this makes GAC uneconomic when MTBE is present above a few tens of parts per billion.

Aeration is an alternative method of treatment for the removal of MTBE from water supplies. Aeration does not have the problem of saturation of an adsorptive medium. However, the relatively low volatility of MTBE makes it difficult to remove compared to the other components of gasoline. Here the Henry's Law Constant is the controlling variable: for MTBE it is estimated to be less than 0.05, whereas it is 0.20 and 0.23 for benzene and toluene respectively. However, the efficacy of aeration can be increased by lengthening the aeration time or increasing the air to water ratio.

Lowry Engineering has developed a unique batch aeration system with variable aeration time, which has treated individual domestic water supplies contaminated with more than 200,000 parts per billion total gasoline and MTBE, with the treated water having no detectable hydrocarbons. Several units are now being monitored in the field where they have been performing satisfactorily. We have found that the system is the most effective and secure against breakthrough when contamination of ground water exceeds a few parts per million total gasoline or fuel oil, or more than 50 ppb MTBE.

For further information on treatment see Lowry and Lowry (1985).

Conclusions

1) MTBE is a more soluble and more rapidly spreading ground water contaminant than other components of gasoline.

2) Its presence in spilled gasoline increases dissolved concentrations of gasoline in ground water in the immediate vicinity of the spill to about an order of magnitude above typical values for spills in which there is no MTBE, and

3) It is more difficult to remove from contaminated water than the other components of gasoline.

Discussion of Policy Options

As this work grew out of a regulatory background founded on the need to limit the damage caused by leaking underground storage tanks, it is natural for us to think in terms of what these findings should mean in terms of new policy decisions. The following are a sample. There may be other options, and we are not advocating one option over another. The object of this discussion is to stimulate the reader into thinking of what should be done.

Option 1: MTBE could be abandoned as an additive in gasoline stored underground. Replacement of MTBE by ethanol, methanol or TBA is not, however, likely to improve the
The Human Side of MTBE Contamination.

Several colleagues have commented that MTBE may be useful as a contaminant tracer because it is apparently less toxic, and precedes and travels further than the BTX components. We beg to differ. That opinion forgets the human element of gasoline spills.

The North Berwick spill contaminated the wells of two homes to concentrations an order of magnitude higher than if there had been no MTBE. The young couple in one of those homes had to wait for us to invent a whole new method of water treatment for their household supply. The young family in the other decided that water treatment was not the way to go, and chose instead to truck in water, at considerable expense and nuisance. The fact that MTBE appears to be less toxic than benzene was no consolation to the parents of young children. The anguish these two families underwent cannot be put into words.

The six other homes in North Berwick with only MTBE in their water were worried about when they would get gasoline too. The trauma associated with the contamination of a home water supply is not proportional to the toxicity of the contaminant detected.

References


Acknowledgements

Thanks are due to our chemist colleagues whose diligence helped identify MTBE to begin with, and whose cooperation in analytical work has kept up the flow of data on it, especially to Larry Boston and Susan Murray of the DEP Lab, and Theresa Zibura of the Public Health Lab. Thanks also to Norman Anderson of the Bureau of Health who helped us evaluate the toxicity data. Thanks for feedback from numerous colleagues at the 1986 NWWA/API Conference on Petroleum and Organic Chemicals in Ground Water. Finally thanks to ARCO for sharing some of their information on MTBE and cooperating on analytical matters.

Bibliographic Sketches

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Peter holds a bachelor's degree in geology from the University of Leicester (UK) and a PhD from Johns Hopkins University. He is currently the senior geologist for oil and hazardous waste programs in Maine. His responsibilities include technical advice to licensing, enforcement and superfund personnel, and evaluation of ground water contamination at sites across the state. His publications in the field have ranged from technical papers to a layman's guide to risk assessment and a wall chart on the Threats to Groundwater in Maine.

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Marcel holds a Bachelor's degree in geology from Williams College and a Master's degree in oceanography from the University of Maine. He has served as the staff person for Maine's Board of Underground Oil Storage System Inspectors, which he was instrumental in founding as part of Maine's underground oil storage program. He is a nationally recognized speaker on underground tank issues, and has participated in EPA workshops formulating a national underground tank strategy. In 1984 he received a German Marshall Fund Fellowship to study European underground oil storage technologies. He is presently an independent consultant providing a broad range of informational and advisory services in the fields of underground petroleum storage technology, management and regulation.

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Jerry obtained his PhD in Environmental Engineering from the University of Kansas in 1978. Since then he has been at the University of Maine researching the removal of volatile contaminants from water supplies, such as naturally-occurring radon, as well as gasoline, MTBE and other solvents. This work has led to the development of a patented treatment system for households which is currently being marketed through Lowry Engineering (948-3790).