

## **Methyl *tert*-Butyl Ether (MTBE) Contamination in Private Wells near Gasoline Stations in Upstate New York**

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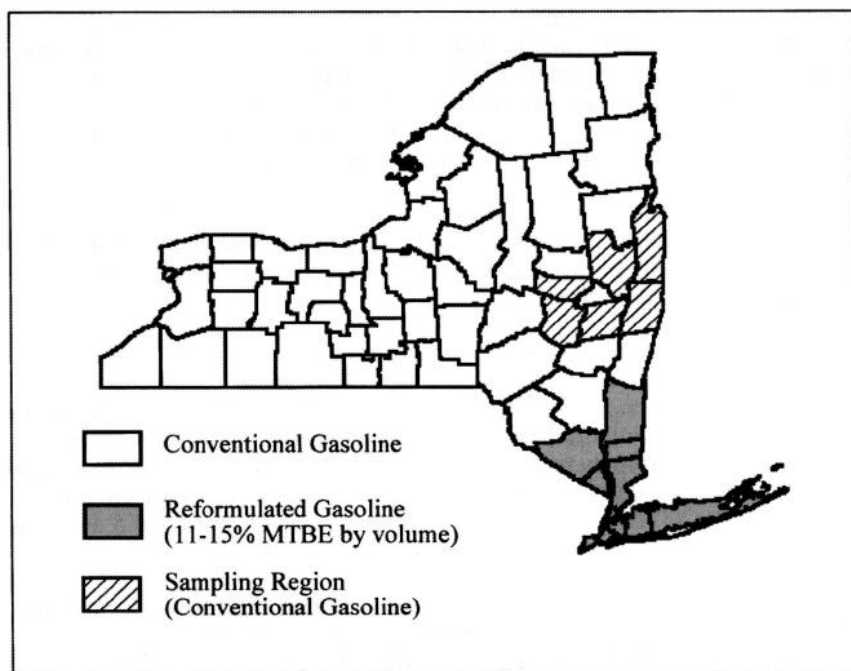
Methyl *tert*-butyl ether (MTBE) belongs to a class of oxygen containing compounds termed "fuel oxygenates" that are added to gasoline to enhance octane and reduce carbon monoxide levels in automobile exhaust. MTBE was first introduced in 1979 as an octane replacement for lead in premium grade gasolines (Bass and Sylvia 1992). In spite of its relatively recent introduction, MTBE has been widely detected in urban groundwater (Squillace et al. 1996). As a groundwater contaminant, MTBE is highly mobile and persistent, resisting both biotic and abiotic forms of degradation (Yeh and Novak 1994 and 1995; Squillace et al. 1997).

The Clean Air Act of 1990 mandates the use of reformulated gasoline (RFG) or Oxygenated Gasoline (Oxyfuel), oxygenated fuels that meet specific content requirements including a minimum percentage of oxygen, in areas with high levels of ozone and carbon monoxide. Currently, 32 areas participate in the RFG program across 18 states (US EPA 1997). MTBE, which is used in 84% of all RFG, comprises 11-15% of RFG by volume (US EPA 1997).

In New York State, several counties in and around New York City and Long Island participate in either the RFG or Oxyfuel programs with conventional gasoline used in the remaining counties (Figure 1). Although conventional gasoline may contain MTBE, it is usually present only in premium grade gasolines and then at relatively low concentrations ranging from 2-8% by volume (Hutcheon et al. 1996). In areas that participate in the RFG program, MTBE is added to all grades of gasoline at concentrations ranging from 11-15% by volume, when MTBE is used as the fuel oxygenate (Squillace et al. 1996).

Of the estimated 73 million people living in areas where MTBE is used in RFG, an estimated 6.4% live near gasoline stations (Brown 1996). How many of these people get their drinking water from private wells is unknown. Private wells lack the protection many public drinking water supplies enjoy through restrictive zoning and routine testing. Additionally, private wells near gasoline stations have are susceptible to potentially large volumes of gasoline through underground storage tanks that may be leaking.

This paper presents data on the frequency of occurrence of MTBE in private wells near gasoline stations versus private wells not near a gasoline station. Additional analyses on the concurrence of MTBE and the BTEX hydrocarbons (benzene, toluene, ethylbenzene, and xylenes) are also presented. The direction of groundwater flow was estimated using local topography at each site.



**Figure 1: Sample Region and Reformulated Gasoline Program Participation in New York State.**

## MATERIALS AND METHODS

The study design is a comparison of the frequency that MTBE was found in private wells considered at risk for contamination, against the frequency that MTBE was found in private wells considered not at risk. Wells were considered at risk if they were down gradient and closer than 0.5 miles from a gasoline station (experimental group). Wells were considered not at risk if they were up gradient and greater than 1.5 miles from a gasoline station (control group).

Using 1994 New York State Office of Real Property Services data, the locations of “gasoline and service stations” and “minimarts” were mapped on a geographic information system in a seven county region surrounding Albany, NY. This map was overlaid on a second, thematic map generated using 1990 Census data that showed the percentage of households on public water by census block.

A total of 78 “gasoline and service stations” and “minimarts” in census blocks with low percentages of public water ( $\leq 20\%$ ) were assigned unique identifiers. Thirty-six of 78 gasoline stations were randomly selected for a site evaluation. Facilities qualified for sampling if there were homes or businesses with private wells nearby and the facility sold gasoline. Eleven of 36 gasoline stations met the criteria for sampling. Facilities failed for two reasons: (1) no gasoline (minimarts without gas or service stations that only repaired automobiles) or (2) no private wells nearby. Most facilities failed due to the former.

A maximum of four, and a minimum of two, private wells were sampled per gasoline station. Where more than four private wells were available, wells were chosen based on their location relative to the direction of groundwater flow, which was estimated using local topography. Wells considered down gradient from the gasoline station were given highest sampling preference. Likewise, wells closer to the gasoline station were sampled before wells farther away.

A total of 42 wells sampled at eleven gasoline stations comprised the experimental group. At each gasoline station, one private well farther than 1.5 miles and up-gradient was selected as a control. Eleven control wells were sampled, one per gasoline station.

Twenty sampling trips were required from early March to mid-June 1997. Samples were drawn from indoor or outdoor taps in homes or businesses before any water treatment systems such as water softeners or filtration units. The water was allowed to run for a few minutes prior to sampling to allow for an ambient groundwater sample. Samples were stored in 40 mL amber vials at 4°C in an iced cooler. Vials for ketone analysis contained no preservatives; vials for volatile organic compounds (VOCs) contained 8 to 20 mg of ascorbic acid and 5 drops of 1:1 hydrochloric acid, added at the time of sampling, as a preservative.

Trip blanks for ketones and VOCs accompanied each sampling trip. Each 40 mL amber trip blank vial was filled with pure reagent water in the laboratory, closed, and carried to and from the laboratory along with other sample vials during sample collections. Samples and trip blanks were delivered to the New York State Department of Health's Wadsworth Center the same sampling day. Two laboratory blanks were included with each analysis. Laboratory blanks were prepared in the laboratory where analysis occurred using purified water.

Samples were analyzed for 57 VOCs using EPA method 502.2. MTBE analysis followed a modified EPA method 8015. A purge-and-trap gas chromatograph with a flame ionization detector was used for MTBE analysis. A MTBE detection limit of 1.0 microgram per liter ( $\mu\text{g/L}$ ) was used throughout the study. Only those VOCs relative to gasoline contamination will be reported in this paper.

## RESULTS AND DISCUSSION

Eight of forty (20.0%) private wells considered at risk for MTBE contamination had detectable concentrations of MTBE at or above the detection limit (1.0  $\mu\text{g/L}$ ). None of eleven control wells had detectable concentrations of MTBE (Table 1). No MTBE was detected in any trip or laboratory blank. These results indicate that private wells near gasoline stations are at risk for low-level MTBE contamination.

The average of the 8 MTBE detections was 10.0  $\mu\text{g/L}$ , with a standard deviation of 20.8  $\mu\text{g/L}$ . Concentrations ranged from less than 1.0  $\mu\text{g/L}$  to 61  $\mu\text{g/L}$ . The median and mode for the detections were 1  $\mu\text{g/L}$ .

Only three private wells had contamination above the detection limit. Two of these, 4 and 61  $\mu\text{g/L}$  MTBE respectively, were near one gasoline station with a leaking underground storage tank. Follow-up sampling of the third well, which had 10  $\mu\text{g/L}$  MTBE in the initial sample, showed decreasing levels of MTBE from 10  $\mu\text{g/L}$  to 6  $\mu\text{g/L}$ , and 1  $\mu\text{g/L}$  over a two month period. The homeowner

**Table 1:** Summary of MTBE Found in Private Wells

	MTBE Concentration (µg/L)	number of detections
Experimental	Non-detections <sup>1</sup>	30
	1	5
	4	1
	10	1
	61	1
Ctrl	Non-detections	11

<sup>1</sup> Detection limit 1.0 µg/L

requested no follow-up sampling after these samples. It is believed these detections were the result of a small-volume gasoline spill that occurred locally.

The generally low concentration of MTBE found suggests non-point sources of contamination such as stormwater runoff and atmospheric transport were major contributors. Recent research has shown that both stormwater runoff and atmospheric transport are non-point contributors of MTBE to the environment (Pankow et al. 1997; Delzer et al. 1996). Point source contamination, from a leaking UST, was positively identified at only one gasoline station.

MTBE was found concurrent with the BTEX hydrocarbons, in only one well. The fact that MTBE, which is used almost exclusively to oxygenate gasoline, was found absent other gasoline-related compounds in 7 of 8 wells is an indication of MTBE's mobility and persistence in the subsurface and the comparative lack of those characteristics in the BTEX compounds.

BTEX hydrocarbons biodegrade more quickly in the subsurface than MTBE and move more slowly (Squillace et al. 1997; Zogorski et al. 1996). The ability of MTBE to travel significant distances and last for long periods in the subsurface has important implications for public officials who rely on BTEX hydrocarbons to alert them to gasoline contamination. Relying solely on BTEX hydrocarbons is to risk missing the presence of potentially significant levels of MTBE that may have traveled from distant sources.

Although the large majority of MTBE detections were low-level, sampling occurred in the Capital Region of New York State: a region of low MTBE use. As with other areas that use conventional gasoline, MTBE is usually found only in premium grade gasolines, and then at relatively low concentrations (2-8% by volume). In regions of RFG/Oxyfuel use, MTBE concentrations are more than doubled and MTBE is added to all grades of gasoline, not just premium, which constitutes a relatively small percentage of gasoline sold. The effect of this significant increase in the occurrence and concentration of MTBE on private wells near gasoline stations in those areas is unknown.

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