RELATIONS BETWEEN THE DETECTION OF METHYL TERT-BUTYL ETHER (MTBE) IN SURFACE AND GROUND WATER AND ITS CONTENT IN GASOLINE

By

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Methyl *tert*-butyl ether (MTBE) is commonly used today in the United States as an octane enhancer and oxygenate in gasoline. Octane enhancement began in the late 1970’s with the phase-out of tetraethyl lead from gasoline. The use of oxygenates was expanded as a result of the enactment of the Clean Air Act (CAA) Amendments of 1990. The CAA Amendments mandate that oxygen must be added to gasoline in areas that do not meet National Ambient Air Quality Standards (NAAQS) for carbon monoxide and ozone. Two primary areas of oxygen use were specified by the CAA Amendments: 1) the Oxygenated Fuels Program (OXY) in which gasoline must contain 2.7% oxygen by weight during the cold season in areas that fail to meet NAAQS for carbon monoxide, and 2) the Reformulated Gasoline Program (RFG) in which gasoline must contain 2% oxygen by weight year-round in areas having the highest levels of tropospheric ozone.

Although the CAA Amendments do not specify which oxygenate must be added to gasoline, the one used most commonly is MTBE. To meet the oxygen requirements of the CAA Amendments, gasoline in designated OXY areas must contain 15% MTBE by volume during the cold season and gasoline in designated RFG areas must contain 11% MTBE by volume year-round. Some areas of the country that meet NAAQS have chosen to voluntarily use RFG while some OXY and RFG areas use higher volumes of MTBE in gasoline than 15 or 11%. Because of its widespread usage, MTBE is manufactured in great quantities with almost 12 billion liters produced in the U.S. in 1998.

The combination of the large-scale use of MTBE and its high solubility, low soil adsorption, and low biodegradability, has resulted in its detection in many ground- and surface-water systems. Sampling of ground water at a national scale by the U.S. Geological Survey’s (USGS) National Water-Quality Assessment (NAWQA) Program between 1993 and 1998 indicated a frequent detection of low concentrations of MTBE. The samples were obtained from a variety of confined and unconfined aquifers and from wells with a variety of water uses. Also, some samples are from studies of ground-water quality in specific land use areas such as urban and agricultural whereas others represent broad assessments of regional aquifers. For ground water, detection of MTBE appears to be related to its usage patterns in gasoline. In ground water, MTBE was detected in about 21% of samples in areas that use substantial (> 5% by volume in gasoline) amounts of MTBE (generally either RFG or OXY areas) and about 2% of samples in areas that do not use substantial (≤ 5% by volume in gasoline) amounts of MTBE. The minimum concentration used to compute frequency of detection in this analysis was 0.2 micrograms per liter (µg/L).

MTBE also has been detected in surface water sampled by the NAWQA Program. In general, the NAWQA surface-water samples were collected in small, perennial streams in urban areas that do not receive large wastewater effluent discharges. In samples taken from 12 urban areas between 1996 and 1998, about 35% contained detectable concentrations of MTBE (minimum reporting concentration varied from 0.1 to 1.0 μg/L). At least one sample from 10 of the 12 urban areas had a detectable concentration of MTBE. As in ground water, the occurrence of MTBE in surface water is related to the use of MTBE in gasoline. At least 76% of the samples in which MTBE was detected were collected from within a designated RFG or OXY area. MTBE also has been detected in urban storm water with about 7% of samples collected by the USGS between 1991 and 1995 containing detectable concentrations of MTBE (minimum reporting concentrations of 0.2 or 1.0 μg/L). As with other data from ground water and surface water, MTBE detection in urban stormwater was related to usage patterns of the compound.

MTBE also has been detected in drinking water in some areas of the country. Of 1,190 community water systems sampled in 12 northeastern states, MTBE was detected in one or more samples in about 7% of the systems at a minimum reporting concentration of 1.0 μg/L. MTBE was detected in about 7% of systems that are supplied exclusively by ground water and about 6% of the systems that are supplied exclusively by surface water. The frequency of occurrence of MTBE is related to the usage patterns of MTBE in gasoline.

Although MTBE detections are related to factors such as population density and primary land use, the occurrence of MTBE in surface and ground water is most strongly related to its use in gasoline. In fact, when several variables are considered in a multivariate regression model, the probability of a detection of MTBE in ground water is highest when an MTBE-use variable is present. Multivariate logistic regression analyses have shown that including use of MTBE in gasoline as a variable results in a 4- to 6-fold increase in probability of detecting MTBE in ground water.

Usage of MTBE can be described in several ways. In general, most RFG areas use MTBE, whereas most OXY areas use another oxygenate. However, this generalization is not useful for determining specific relations between MTBE detection and MTBE use. Data on the specific volumetric content of MTBE in gasoline can help to more accurately quantify MTBE use in gasoline in certain areas. The National Institute for Petroleum and Energy Research (NIPER) Survey reports MTBE content (as percent by volume) in gasoline from samples taken at selected service stations throughout the country. The content of MTBE is seasonal, particularly in OXY areas, and can vary in many locations. However, NIPER data provides a fairly clear picture of MTBE usage in selected urban areas for the last ten years.

Using NIPER data, areas of the country where NAWQA has sampled surface and ground water were classified into two MTBE use categories: 1) high MTBE use and 2) low/no/unknown MTBE use. High MTBE use areas were defined as areas where MTBE content in gasoline was an average of > 2% (> 6% for seasonal use only) by volume for the entire period of record, whereas low/no/unknown MTBE use areas were defined as areas where MTBE content in gasoline was an average of ≤ 2% by volume for the entire period of record or was unknown. Areas where MTBE content in gasoline was an average of ≤ 2% by volume may be using MTBE for octane enhancement only. These areas can then also be arranged into RFG, OXY or other (no NAAQS nonattainments) areas based on air-quality requirements. By comparing detection frequencies between MTBE use categories within each air-quality requirement area, it is possible to gain insight into the relation between the detection of MTBE and its use. Figures 1 and 2 illustrate the differences in percent detection of MTBE in ground and surface water for both MTBE use categories within each federally-mandated oxygenate use area.

The use of MTBE, as opposed to another oxygenate, in either RFG or OXY areas results in a significant increase in the detection frequency of MTBE in both surface and ground water (figs. 1 and 2). In fact, for ground water, the use of MTBE in RFG and OXY areas results in an increase in the detection frequency of MTBE of 4 and 8 times, respectively (fig. 1). Even in areas other than those designated as RFG or OXY, the use of MTBE results in a 3-fold increase in the detection frequency of MTBE in ground water. For surface water, the use of MTBE in RFG and OXY areas results in an increase in the detection frequency of MTBE of 18 and 2 times, respectively. However, for areas other than RFG or OXY, the frequency of detection of MTBE in surface water is lower for areas that use MTBE compared to areas where either no MTBE is used or its use is unknown. This apparent anomaly may be, in part, the result of the uncertainty involved in assigning an MTBE-use category to relatively large geographic areas such as surface-water drainage basins that may cross MTBE-use boundaries.

A more detailed analysis of the relations between the content of MTBE in gasoline and the detection frequency of MTBE in ground and surface water can be performed by using the percent by volume of MTBE in gasoline provided by NIPER. Frequencies of detection of MTBE were compared to percent volumes of MTBE in gasoline for selected metropolitan areas where NAWQA sampled surface and ground water (figs. 3 and 4). For ground water, 21 metropolitan areas had information on detection frequency and percent volume of MTBE in gasoline, whereas for surface water only 9 metropolitan areas had this information. Each data point on figures 3 and 4 represents a different metropolitan area. Table 1 lists the metropolitan areas represented in figures 3 and 4.

The frequencies of detection of MTBE in figures 3 and 4 were computed using no specified minimum reporting concentration for MTBE (i.e., all detectable concentrations were used to compute detection frequencies). For each metropolitan area, the frequencies of detection of MTBE were used in this analysis only if at least 10 samples were analyzed for MTBE. The percent volume of MTBE in gasoline shown in these figures was obtained for each metropolitan area by computing a long-term arithmetic mean of MTBE content (percent by volume) for all gasoline samples prior to the latest year of water sampling. For ground water, three cities -- Columbia, SC, Harrisburg, PA, and Norfolk, VA -- had values of MTBE in gasoline for only 2 sampling periods and had a total of less than 20 samples each. For surface water, Columbia, SC, had values of MTBE in gasoline for only 2 sampling periods.

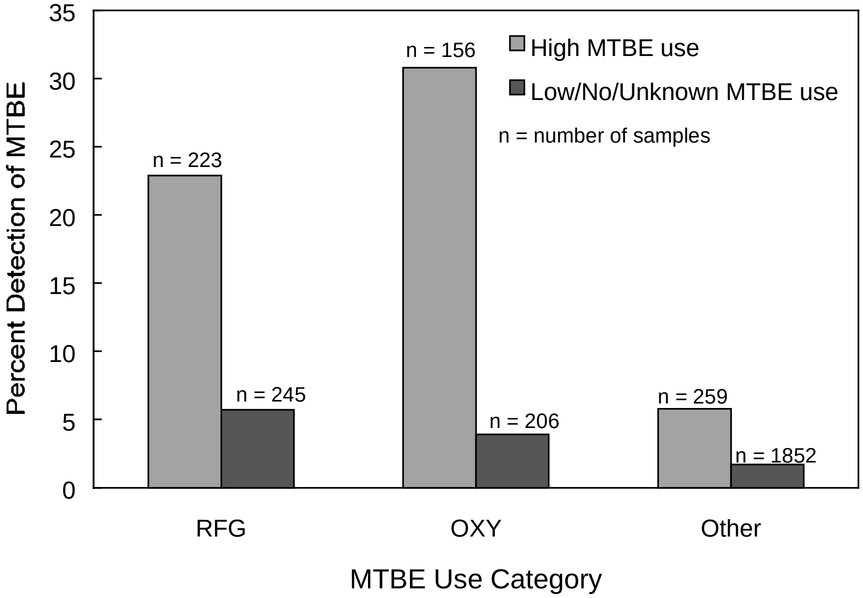

Figure 1. Frequency of detection of MTBE in samples of ground water (1993-1998) by MTBE use categories.

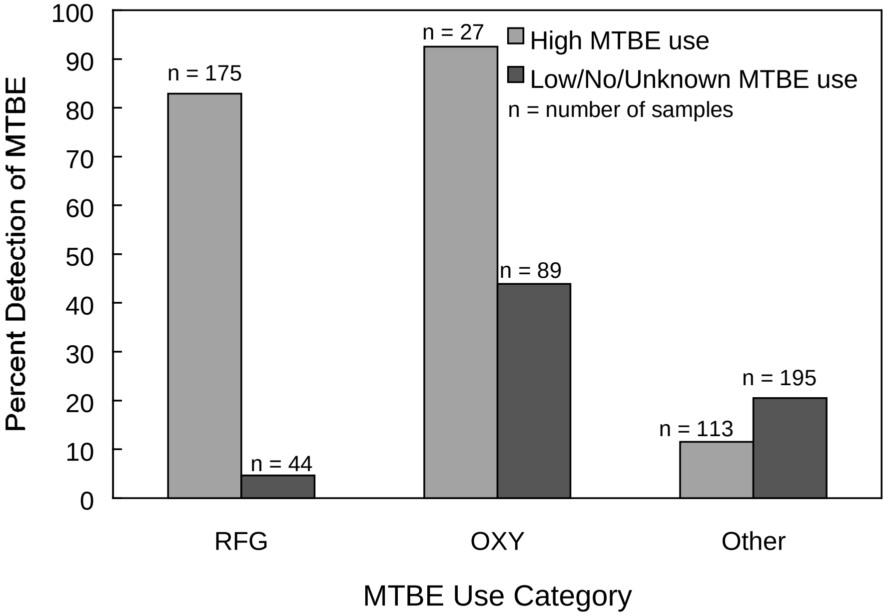

Figure 2. Frequency of detection of MTBE in samples of surface water (1996-1998) by MTBE use categories.

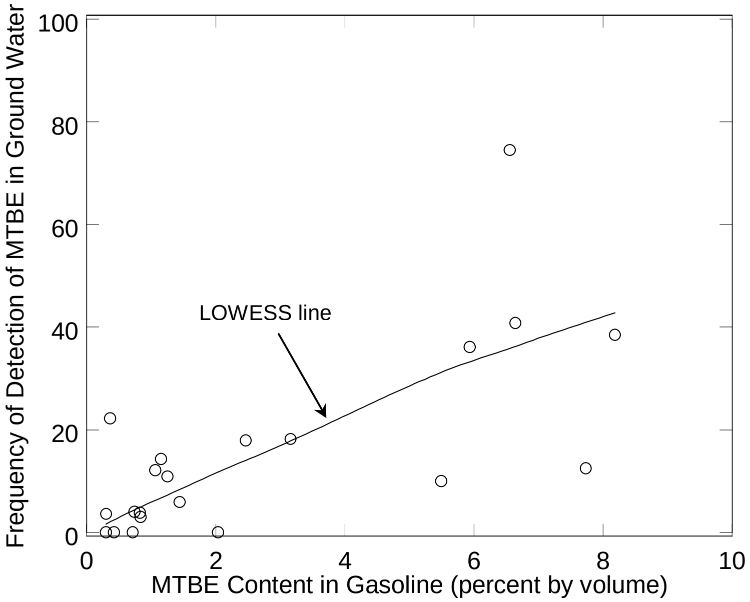

Figure 3. Detection frequency of MTBE in ground water versus MTBE content in gasoline.

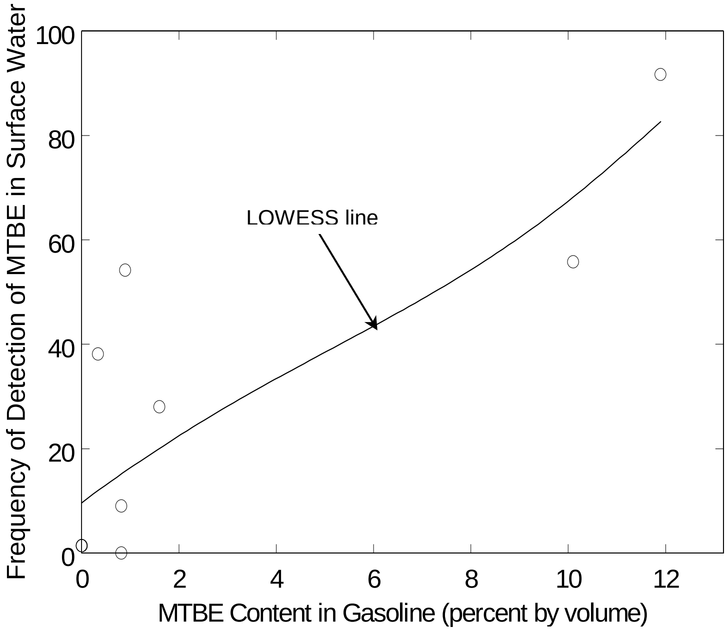

Figure 4. Detection frequency of MTBE in surface water versus MTBE content in gasoline.

Table 1. Metropolitan areas where NAWQA has sampled ground and surface water for MTBE and where data exists on MTBE content in gasoline.

Ground Water	Surface Water
Albuquerque, NM	Columbia, SC
Atlanta, GA	Detroit-Flint, MI
Columbia, SC	Memphis, TN
Dallas-Fort Worth, TX	Minneapolis-St. Paul, MN
Denver, CO	New York, NY
Harrisburg, PA	Philadelphia, PA
Hartford, CT	Pittsburgh, PA
Indianapolis, IN	San Antonio, TX
Las Vegas, NV	Seattle, WA
Memphis, TN	
Miami, FL	
Minneapolis-St. Paul, MN	
New York, NY	
Norfolk, VA	
Philadelphia, PA	
Phoenix, AZ	
Portland, OR	
Reno, NV	
San Antonio, TX	
Seattle, WA	
Tampa-St. Petersburg, FL	

The LOcally WEighted Scatterplot Smoothing (LOWESS) lines in figures 3 and 4 represent predicted values of the response variable (frequency of detection of MTBE) based on the input variable (MTBE content in gasoline) using a weighted least squares regression. A LOWESS line aids in emphasizing how the two variables are related without assuming a linear relation. The smoothness factor (f), or span, used for the line was 0.75 in figure 3 and 1.0 in figure 4.

The LOWESS line in figure 3 indicates that increasing frequency of detection of MTBE in ground water in 21 metropolitan areas is related to increasing MTBE content in gasoline. Although the variability in MTBE frequency of detection seems to increase as MTBE content in gasoline increases, the general trend is clear. For surface water (fig. 4) the relation seems more pronounced and is related to the higher detection frequencies in surface water in high use areas.

The relations illustrated in figures 3 and 4 indicate that the frequency of detection of MTBE in surface and ground water has a positive relation to content of MTBE in gasoline. As the NAWQA program gathers more data, understanding of the relations between MTBE detection in water and various explanatory factors will be enhanced. Although the shape and slope of the LOWESS lines shown in these figures may change as more data are gathered, it is believed that the general trend in the data will not.

It is apparent that the occurrence of the fuel additive MTBE in ground and surface water is related to its use in gasoline. The frequency of detection of MTBE is higher in areas that use greater amounts of MTBE in gasoline. In fact, there is a 2- to 18-fold increase in the detection frequency of MTBE in surface water, and a 3- to 8-fold increase for ground water, in RFG or OXY areas that use MTBE as a gasoline oxygenate. As the percent by volume of MTBE in gasoline increases, the frequency of detection of MTBE in ground and surface water increases. Even at relatively low content of MTBE in gasoline (≤ 2 %), such as areas in which it is used only as an octane enhancer, the frequency of detection of MTBE in surface water can be significant.