



**NATIONAL WATER-QUALITY ASSESSMENT PROGRAM
NATIONAL SYNTHESIS ON VOLATILE ORGANIC COMPOUNDS**

Occurrence and Implications of Methyl *tert*-Butyl Ether and Gasoline Hydrocarbons in Ground Water and Source Water in the United States and in Drinking Water in 12 Northeast and Mid-Atlantic States, 1993-2002

Water-Resources Investigations Report 03-4200

U.S. Department of the Interior
U.S. Geological Survey

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By Michael J. Moran, John S. Zogorski, and Paul J. Squillace

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U.S. Department of the Interior

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FOREWORD

The U.S. Geological Survey (USGS) is committed to providing the Nation with accurate and timely scientific information that helps enhance and protect the overall quality of life and that facilitates effective management of water, biological, energy, and mineral resources (<http://www.usgs.gov/>). Information on the quality of the Nation's water resources is critical to assuring the long-term availability of water that is safe for drinking and recreation and suitable for industry, irrigation, and habitat for fish and wildlife. Population growth and increasing demands for multiple water uses make water availability, now measured in terms of quantity and quality, even more essential to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program in 1991 to support national, regional, and local information needs and decisions related to water-quality management and policy (<http://water.usgs.gov/nawqa>). Shaped by and coordinated with ongoing efforts of other Federal, State, and local agencies, the NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are the conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues and priorities.

From 1991-2001, the NAWQA Program completed interdisciplinary assessments in 51 of the Nation's major river basins and aquifer systems, referred to as Study Units (<http://water.usgs.gov/nawqa/studyu.html>). Baseline conditions were established for comparison to future assessments, and long-term monitoring was initiated in many of the basins. During the next decade, 42 of the 51 Study

Units will be reassessed so that 10 years of comparable monitoring data will be available to determine trends at many of the Nation's streams and aquifers. The next 10 years of study also will fill in critical gaps in characterizing water-quality conditions, enhance understanding of factors that affect water quality, and establish links between sources of contaminants, the transport of those contaminants through the hydrologic system, and the potential effects of contaminants on humans and aquatic ecosystems.

The USGS aims to disseminate credible, timely, and relevant science information to inform practical and effective water-resource management and strategies that protect and restore water quality. We hope this NAWQA publication will provide you with insights and information to meet your needs, and will foster increased citizen awareness and involvement in the protection and restoration of our Nation's waters.

The USGS recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for a fully integrated understanding of watersheds and for cost-effective management, regulation, and conservation of our Nation's water resources. The NAWQA Program, therefore, depends on advice and information from other agencies—Federal, State, interstate, Tribal, and local—as well as nongovernmental organizations, industry, academia, and other stakeholder groups. Your assistance and suggestions are greatly appreciated.

Robert M. Hirsch
Associate Director for Water

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Occurrence and Implications of Methyl *tert*-Butyl Ether and Gasoline Hydrocarbons in Ground Water and Source Water in the United States and in Drinking Water in 12 Northeast and Mid-Atlantic States, 1993-2002

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ABSTRACT

The occurrence and implications of methyl *tert*-butyl ether (MTBE) and gasoline hydrocarbons were examined in three surveys of water quality conducted by the U.S. Geological Survey—one national-scale survey of ground water, one national-scale survey of source water from ground water, and one regional-scale survey of drinking water from ground water. The overall detection frequency of MTBE in all three surveys was similar to the detection frequencies of some other volatile organic compounds (VOCs) that have much longer production and use histories in the United States. The detection frequency of MTBE was higher in drinking water and lower in source water and ground water. However, when the data for ground water and source water were limited to the same geographic extent as drinking-water data, the detection frequencies of MTBE were comparable to the detection frequency of MTBE in drinking water. In all three surveys, the detection frequency of any gasoline hydrocarbon was less than the detection frequency of MTBE. No concentration of MTBE in source water exceeded the lower limit of U.S. Environmental Protection Agency's Drinking-Water Advisory of 20 µg/L (micrograms per liter). One concentration of MTBE in ground water exceeded 20 µg/L, and

0.9 percent of drinking-water samples exceeded 20 µg/L.

The overall detection frequency of MTBE relative to other widely used VOCs indicates that MTBE is an important concern with respect to ground-water management. The probability of detecting MTBE was strongly associated with population density, use of MTBE in gasoline, and recharge, and weakly associated with density of leaking underground storage tanks, soil permeability, and aquifer consolidation. Only concentrations of MTBE above 0.5 µg/L were associated with dissolved oxygen. Ground water underlying areas with high population density, ground water underlying areas where MTBE is used as a gasoline oxygenate, and ground water underlying areas with high recharge has a greater probability of MTBE contamination. Ground water from public-supply wells and shallow ground water underlying urban land-use areas has a greater probability of MTBE contamination compared to ground water from domestic wells and ground water underlying rural land-use areas.

INTRODUCTION

The Clean Air Act (CAA) Amendments of 1990 specified that oxygen must be added to gasoline in areas where air-quality standards have not been

attained (U.S. Environmental Protection Agency, 1990). Oxygenates are compounds that contain oxygen and are added to gasoline in order to meet the requirements of the CAA Amendments. Since the late 1980s, oxygenates have been used in gasoline in areas regulated under the Reformulated Gasoline (RFG) and Oxygenated Fuel (Oxyfuel) Programs of the CAA Amendments. As of 1998, approximately 30 percent of all gasoline in the United States contained oxygenates for compliance with RFG requirements and an additional 4 percent contained oxygenates for compliance with Oxyfuel requirements (U.S. Environmental Protection Agency, 1998).

Although the CAA Amendments did not specify which oxygenate must be added to gasoline to achieve oxygen requirements, the alkyl ether methyl *tert*-butyl ether (MTBE) has been, and continues to be, the most commonly used oxygenate. As of 1998, MTBE was used in more than 80 percent of oxygenated gasoline. Recent information indicates that MTBE is the most frequently used gasoline oxygenate in RFG areas (U.S. Environmental Protection Agency, 2003a), whereas ethanol is the most frequently used gasoline oxygenate in Oxyfuel areas (U.S. Environmental Protection Agency, 2003b). In addition to its use as a gasoline oxygenate, MTBE also has been widely used to enhance octane in gasoline (U.S. Environmental Protection Agency, 1998).

Since about 1991, large volumes of MTBE have been produced every year in the United States and used as a gasoline oxygenate. In 2001, production of MTBE in the United States was over 12 billion liters (Department of Energy, 2002). From 1993 to 1998, MTBE was the second most-produced organic chemical in the United States (U.S. Environmental Protection Agency, 1998).

A chemical with such large production and widespread use has a substantial potential of release to the environment. Once released to the environment, MTBE can be transported to ground-water resources through a variety of mechanisms. Once in ground water, MTBE concentrations can adversely affect the quality of water from aquifers that are used to supply water for private household wells or public water-supply systems.

MTBE has been detected in ground water in the United States and other countries such as Germany (Klinger and others, 2002; Moran, Clawges, and Zogorski, 2002; Moran, Lapham, and others, 2002). MTBE also has been found in some reservoirs and

rivers that are used as public water supplies (Grady, 2003). Recent data show the presence of MTBE in ground water used as a source for drinking water (Grady, 2003) and in drinking water in the United States (Grady and Casey, 2001; Williams and others, 2002).

Although the magnitude of the problem is not known, contamination of ground water used as a source for drinking water already has resulted in the closure of many drinking-water wells around the country including both public and private wells. MTBE in drinking water may have possible human health consequences including carcinogenic potential and detrimental reproductive and developmental effects (Hartley and others, 1999). The U.S. Environmental Protection Agency (1997) has issued a drinking-water advisory suggesting that MTBE concentrations be less than 20 to 40 µg/L in drinking water (micrograms per liter).

Research has shown that detections of MTBE in ground water are more frequent in areas where MTBE is used as a gasoline oxygenate, such as RFG or Oxyfuel areas, in comparison to areas where it is not used as a gasoline oxygenate (Moran, Clawges, and Zogorski, 2002). However, MTBE also has been detected in ground water in many other areas of the Nation outside of the RFG and Oxyfuel areas. The geographically widespread detection of MTBE indicates that ground water in many areas may be at potential risk of MTBE contamination (Moran, Clawges, and Zogorski, 2002).

Purpose and Scope

The purpose of this report is to describe the occurrence and implications of MTBE and gasoline hydrocarbons in ground water, source water, and drinking water from data collected or compiled by the U.S. Geological Survey's (USGS) National Water-Quality Assessment (NAWQA) Program and cooperators. In this report, gasoline hydrocarbons refers to a select group of volatile organic compounds (VOCs) whose primary use is believed to be in gasoline and includes the BTEX (benzene, toluene, ethylbenzene, and xylenes) compounds as well as naphthalene, *n*-butylbenzene, *iso*-propylbenzene, styrene, and 1,2,4-trimethylbenzene. Although these VOCs are components of gasoline, they do have other domestic, com-

mercial, and industrial uses, and they may have other sources to ground water in addition to gasoline.

This report provides an overview for the entire Nation of the occurrence of MTBE in ground water and ground water that is withdrawn for human consumption prior to any treatment (hereafter referred to as source water). The occurrence of MTBE in drinking water in 12 Northeast and Mid-Atlantic States also is examined. The focus of this report is on the occurrence and concentrations of MTBE and gasoline hydrocarbons in these media, and on the occurrence of MTBE in areas where MTBE content in gasoline is used as a surrogate for MTBE input to the environment. The implications of the occurrence of MTBE and gasoline hydrocarbons in these media also are described. This report also describes other factors that are associated with the occurrence of MTBE in ground water and that may aid in understanding the sources and pathways of MTBE to ground water and the vulnerability of aquifers to MTBE contamination.

Data and Methods

Extensive data sets were used for analyses in this report. Data were analyzed from three sources: (1) the NAWQA Program that sampled ground water throughout the United States from 1993-2002 as a part of occurrence studies (ground-water survey); (2) a collaborative effort of the NAWQA Program and other organizations in a national survey that sampled ground water used as a source of drinking water throughout the United States from 1999-2000 (source-water survey); and (3) the NAWQA Program that compiled data on drinking water from community water systems (CWSs) in 12 Northeast and Mid-Atlantic States that were sampled from 1993-1998 (drinking-water survey).

As part of NAWQA occurrence studies, personnel collected samples of ground water between 1993 and 2002. These samples were analyzed for MTBE and other VOCs at the USGS National Water-Quality Laboratory (NWQL). The ground-water occurrence studies of NAWQA included two main components: (1) major aquifer surveys of water quality in one or more aquifers underlying each NAWQA study area, and (2) land-use studies assessing the quality of ground water underlying agricultural and urban land-use areas (Gilliom and others, 1995). In the major aquifer surveys, NAWQA personnel sampled large areal and depth

dimensions of a principal aquifer that constitutes an important ground-water resource within the study area. In the land-use studies, NAWQA personnel sampled shallow ground water in areas of predominant agricultural or urban land use (Gilliom and others, 1995). Sampling in the land-use studies was designed to target recently recharged ground water generally less than 10 years old.

The design for each of the NAWQA occurrence studies was network-based consisting of the selection of about 30 wells (sampling sites) in an unbiased, random, equal-area distribution throughout the study area. In general, the wells sampled by NAWQA were not located in proximity to known point source releases. As of January 2003, data on MTBE and other VOCs were available for 3,964 wells sampled in the NAWQA occurrence studies. These data constitute the ground-water survey.

Personnel from CWSs throughout the United States collected samples of ground water used as a source of drinking water from 1999 to 2000 as part of a national source-water survey. This survey was a collaborative effort between the American Water Works Association Research Foundation (AWWARF), the Metropolitan Water District of Southern California (MWDSC), the Oregon Health and Sciences University, participating CWSs, and the USGS. The purpose of this survey was to assess the magnitude and spatial extent of MTBE contamination of source water whether derived from surface water or ground water. In this report, only source water from ground water was considered. Two phases of the national source-water survey, with respect to ground water, were accomplished: (1) a random survey of 579 ground-water sources throughout the country, and (2) a focused survey of 78 ground-water sources throughout the country that were known to have MTBE contamination or were considered susceptible to MTBE contamination (Clawges and others, 2001). Detailed results of the random and focused surveys can be found in Grady (2003) and Delzer and Ivahnenko (2003), respectively. In this report, only data from the random survey were used in order to avoid potential bias in the occurrence of MTBE.

The selection of CWSs sampled in the random survey was statistically based and was stratified by population-served size category, source of water (ground water or surface water), and total number of people served (Ivahnenko and others, 2001). For

ground water, all samples were collected prior to treatment and as close as possible to the wellhead. The MWDC laboratory analyzed the samples of source water for MTBE and other VOCs. Data on MTBE were available from a total of 571 samples of ground water. These data constitute the source-water survey.

Data on MTBE and other VOCs in drinking water were compiled by the USGS from various agencies in 12 Northeast and Mid-Atlantic States. Unlike the previous ground-water and source-water surveys, the drinking-water survey was not national in scope and only covered these regions. The purpose of this survey was to describe the occurrence and distribution of MTBE and other VOCs in public drinking water supplied by CWSs in these regions. These regions were selected because they generally are densely populated, have a long-term history of urbanization, and are areas with high use of public-water supply and high use of MTBE in gasoline (Grady and Casey, 2001; Moran and others, 2001). In addition, large parts of these regions are regulated under the RFG Program. A random subset of all CWSs in the regions was selected using a statistical approach that stratified selection by State, source of water, and number of people served (Grady and Casey, 2001).

The data from the 12 Northeast and Mid-Atlantic States represent drinking water that was sampled to meet the requirements of the Safe Drinking Water Act (SDWA). The samples were collected from 1993-98 and were analyzed by a variety of State and private laboratories. The data on drinking water were summarized by system and do not reflect occurrence by source. A CWS was counted as having a detection of MTBE if a measurable concentration of MTBE was reported in one or more water samples associated with any source or sample location for that CWS. In this report, only samples of drinking water obtained from ground-water sources were used for analysis. Data on MTBE and other VOCs were available for a total of 985 CWSs with ground-water sources. These data constitute the drinking-water survey (Grady and Casey, 2001).

Laboratory reporting levels for MTBE and gasoline hydrocarbons varied between and within the surveys. For ground water collected by NAWQA, variability in the laboratory reporting level for MTBE primarily was the result of the introduction of new, information-rich methods and a change in the policy of NWQL in 1996 concerning the determination of

laboratory reporting levels (Rose and Schroeder, 1995; Connor and others, 1998; Oblinger Childress and others, 1999). Laboratory reporting levels for MTBE in ground-water samples ranged from 0.1 to 1.66 $\mu\text{g/L}$ with a median of 0.17 $\mu\text{g/L}$. Laboratory reporting levels for gasoline hydrocarbons ranged from 0.03 to 5 $\mu\text{g/L}$ with a median of 0.1 $\mu\text{g/L}$. Laboratory reporting levels greater than 0.2 $\mu\text{g/L}$ may be the result of dilution of environmental samples or laboratory censoring of data after review of laboratory quality-control (QC) information.

Field QC data collected by the NAWQA Program for the occurrence studies indicated that systematic contamination of environmental samples by MTBE did not occur as a result of collection, processing, handling, and shipping procedures (G.C. Delzer, U.S. Geological Survey, oral commun., 2002). Detections of some gasoline hydrocarbons in field blanks indicated that some systematic contamination by these compounds was suspected (D.A. Bender, U.S. Geological Survey, oral commun., 2002). Environmental samples that were associated with field blanks that had suspected systematic contamination were not used in this analysis.

For source-water samples analyzed by MWDC, the laboratory reporting level for MTBE was constant at 0.078 $\mu\text{g/L}$. However, the laboratory reporting level for the gasoline hydrocarbon compounds differed from this level, ranging from 0.044 to 0.13 $\mu\text{g/L}$ with a median of 0.066 $\mu\text{g/L}$. A review of field QC data indicated systematic low-concentration (<0.2 $\mu\text{g/L}$) contamination of field and trip blanks by various VOCs. As a result, all source-water environmental samples were censored at a level of 0.2 $\mu\text{g/L}$ for all VOCs to ensure that reported concentrations represent environmental concentrations of VOCs and not systematic contamination.

For drinking-water samples, the laboratory reporting level for MTBE ranged from 0.1 to 10 $\mu\text{g/L}$ with a median of 0.5 $\mu\text{g/L}$. The laboratory reporting level for gasoline hydrocarbons also was variable ranging from 0.017 to 1.5 $\mu\text{g/L}$ with a median of 0.245 $\mu\text{g/L}$. The variability in reporting levels in this data set primarily was a result of different censoring criteria and instrument performances of the various State and private laboratories that performed the analyses. For inclusion of drinking-water data in this analysis, collection of field QC data was required to ensure that a minimum standard of data quality was

maintained. It also was required that QC data be used to evaluate and, if necessary, to censor drinking-water data to ensure that reported concentrations represent environmental concentrations of VOCs and not systematic contamination (Grady and Casey, 1999).

In all three surveys, each well, source, or sampling site was allowed to have only one set of environmental data representing a time snapshot of water quality. In most cases, the primary environmental sample taken from the well was analyzed. For NAWQA data, the primary environmental sample represents the first environmental sample taken from the well. If more than one set of environmental water-quality results was available, the most recent set was selected. Therefore, each well, source, or sampling site had only one set of water-quality results. Consequently, the term “sample” is used in this report to indicate the results from a single well, source, or sampling site.

Assessment Level Computations

Data analysis was complicated by the variations in laboratory reporting levels between and within the surveys. In order to accurately compare detection frequencies of MTBE and gasoline hydrocarbons between different data sets that have varying reporting levels, it was necessary to apply a uniform censoring level that is referred to as an assessment level in this report. If a water-quality constituent has reporting levels that vary between data sets, comparisons of detection frequencies between the data sets may not reflect true differences in water quality. Instead, they may simply reflect differences in instrument sensitivity, analytical methods, or censoring levels between the different laboratories.

For comparing the detection frequencies of water-quality constituents with varying laboratory reporting levels, an assessment level should be applied before detection frequencies are computed. The application of an assessment level allows for the most accurate comparison of detection frequencies between data sets with different laboratory reporting levels.

In this report, an assessment level of 0.2 µg/L was applied whenever MTBE detection frequencies were compared between the three surveys. However, if comparisons of detection frequencies were made between subsets of a single survey, or detection frequency was examined wholly within a single survey, no assessment level was applied. To execute the assess-

ment level, analyses with a detectable concentration less than 0.2 µg/L were converted to non-detections. Detection frequency was then computed as the number of samples that had a detected concentration of MTBE greater than or equal to 0.2 µg/L divided by the number of samples with MTBE analyses times 100.

For comparisons of MTBE concentrations between the three surveys, an assessment level of 0.5 µg/L was applied to data for ground water and source water to make the data most comparable to the drinking-water data. This level was selected because the median laboratory reporting level for data from the drinking-water survey is 0.5 µg/L and there are no concentrations below that level in this data set.

Statistical Methods

To better understand the significance of the results and the hydrologic processes that have caused them, statistical tests were performed to evaluate and compare data. The statistical significance level (α) used in this report for all tests was 0.05. The results of some statistical tests are shown graphically as letter symbols in the figures. If two groups of data share the same letter symbol, the null hypothesis was not rejected for that comparison. If two groups of data do not share the same letter symbol, the null hypothesis was rejected for that comparison.

Contingency table tests, using Pearson’s chi-square test of independence, were performed to determine if detection frequencies between one or more surveys, or detection frequencies between subsets of one survey, were independent. Contingency table tests were used because detection frequencies are nominal, categorical variables. The null hypothesis states that the row variables are independent from the column variables. If the null hypothesis is rejected, the row variables are dependent on the column variables and the detection frequencies were considered dependent on the survey.

The nonparametric Mann-Whitney test (Helsel and Hirsch, 1992) was used to compare two independent groups of data such as the population densities around wells between areas of high and low MTBE use in gasoline. The null hypothesis states that the values in one group are not higher than the values in the other group. If the null hypothesis is rejected, the population densities around one group of wells were higher than another.

The nonparametric Kolmogorov-Smirnov test (Helsel and Hirsch, 1992) was used to compare MTBE concentrations between surveys in order to determine if the distributions of concentrations were significantly different. The null hypothesis states that the distributions are not significantly different. If the null hypothesis was rejected, the distributions were considered significantly different. If the distributions of concentrations were significantly different, the concentrations of one distribution was higher or lower than the other.

For determining associations between multiple independent variables and MTBE occurrence, a multivariate logistic regression analysis was used (Helsel and Hirsch, 1992). For water-quality analyses, the explanatory variables selected for analysis are often anthropogenic or hydrogeologic parameters that can provide insight and understanding into the sources, transport processes, or environmental mechanisms that affect contamination. Logistic regression often is used to predict the probability of occurrence of a contaminant as it relates to various explanatory variables. However, in this case the regression results were not intended to provide a capability for predicting the probability of detecting MTBE. Instead they were used to determine associations between MTBE occurrence and explanatory variables and to determine the strength and direction of the associations.

For the overall regression equation, if the overall likelihood produced a p -value of ≤ 0.05 , all explanatory variables were considered significantly associated with the probability of MTBE occurrence. The significance of nested models was tested using the partial likelihood ratio test. For cases where one additional coefficient was added, the Wald statistic p -value was used to determine the significance of the slope coefficient. If the Wald statistic p -value of the slope coefficient was less than 0.05 and the upper and lower bounds of the odds ratio did not include 1, the additional variable was considered significantly associated with the probability of occurrence of MTBE. Non-nested regression analyses were tested using Akaike's Information Criteria (Helsel and Hirsch, 1992). Standardized coefficients were used to compare the strength of a relation between the dependent variable and different explanatory variables. The method for computing standardized slope coefficients followed Menard (2002).

OCURRENCE OF MTBE AND GASOLINE HYDROCARBONS

The geographic distribution of samples analyzed for MTBE in all three surveys is shown in figure 1. The circles in figure 1 represent the locations where samples were collected. The open circles show the location of samples that did not have a detected concentration of MTBE, whereas the filled circles show the location of samples that had a detected concentration of MTBE. In all three surveys combined, 420 samples had detected concentrations of MTBE using no assessment level. This corresponds to an overall detection frequency of 7.6 percent in a total of 5,520 samples. Samples with a detected concentration of MTBE are most intensively represented in the Northeast region of the country (fig. 1).

For gasoline hydrocarbons, the overall detection frequency was 16 percent using no assessment level. One or more gasoline hydrocarbons were detected in 931 of 5,818 total samples. Samples with a detected concentration of one or more gasoline hydrocarbons are less intensively represented in the Northeast region of the country compared to MTBE.

MTBE

The detection frequency of MTBE in each of the three surveys is illustrated in figure 2. Data for ground water and source water were analyzed at an assessment level of 0.2 $\mu\text{g/L}$ to make them comparable to data for drinking water. For ground-water data, the detection frequency is only for MTBE analyses in the major aquifer surveys because this is the best representation of the quality of the ground-water resource. The bold letters in figure 2 graphically display the results of chi-square tests of independence comparing MTBE detection frequencies between the three surveys.

The detection frequency of MTBE was lowest in ground water at 2.9 percent and highest in drinking water at 9 percent (fig. 2). The detection frequency of MTBE in source water was 5.4 percent. The detection frequencies of MTBE were dependent on the survey for all comparisons ($p < 0.05$).

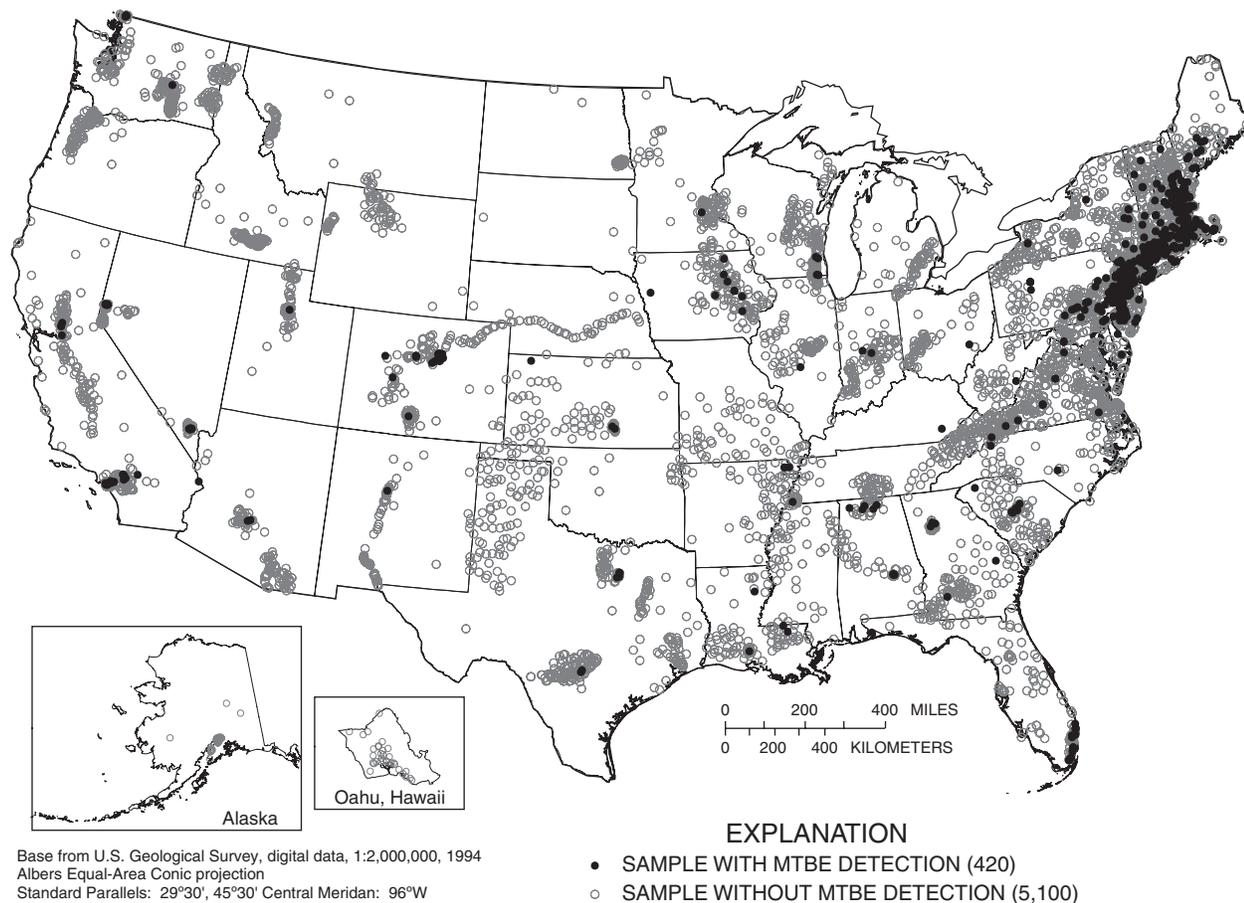


Figure 1. Locations of samples of ground water, source water, and drinking water that were analyzed for MTBE and the locations of samples with detections of MTBE using no assessment level.

Data from the ground-water and source-water surveys also were examined in only the 12 Northeast and Mid-Atlantic States and at an assessment level of 0.5 µg/L to make them comparable to the drinking-water data. For ground water, the detection frequency of MTBE in these regions was 6.6 percent, whereas the detection frequency of MTBE in source water from these regions was 11.3 percent. These detection frequencies were similar to the detection frequency of MTBE in drinking water. In this analysis, the detection frequencies of MTBE were not dependent on the survey for all comparisons ($p < 0.05$).

NAWQA Studies

As indicated previously, NAWQA conducts both major aquifer surveys and land-use studies. The land-use studies examine shallow ground water in areas of

predominant agricultural or urban land use. Figure 3 illustrates the detection frequencies of MTBE in all studies combined, major aquifer surveys, and land-use studies using no assessment level. The detection frequency of MTBE was highest in urban land-use studies at 13 percent and lowest in agricultural land-use studies at 1.2 percent. The detection frequency of MTBE in the major aquifer surveys was intermediate at 2.8 percent. For all of NAWQA studies combined, the detection frequency of MTBE was 4.7 percent.

For various studies of ground-water quality, the NAWQA program samples many different types of wells. Figure 4 illustrates the detection frequencies of MTBE in four different types of wells sampled by the NAWQA Program using no assessment level. Although domestic-supply wells are most frequently sampled by NAWQA for MTBE, the detection frequency of MTBE is highest in monitoring wells.

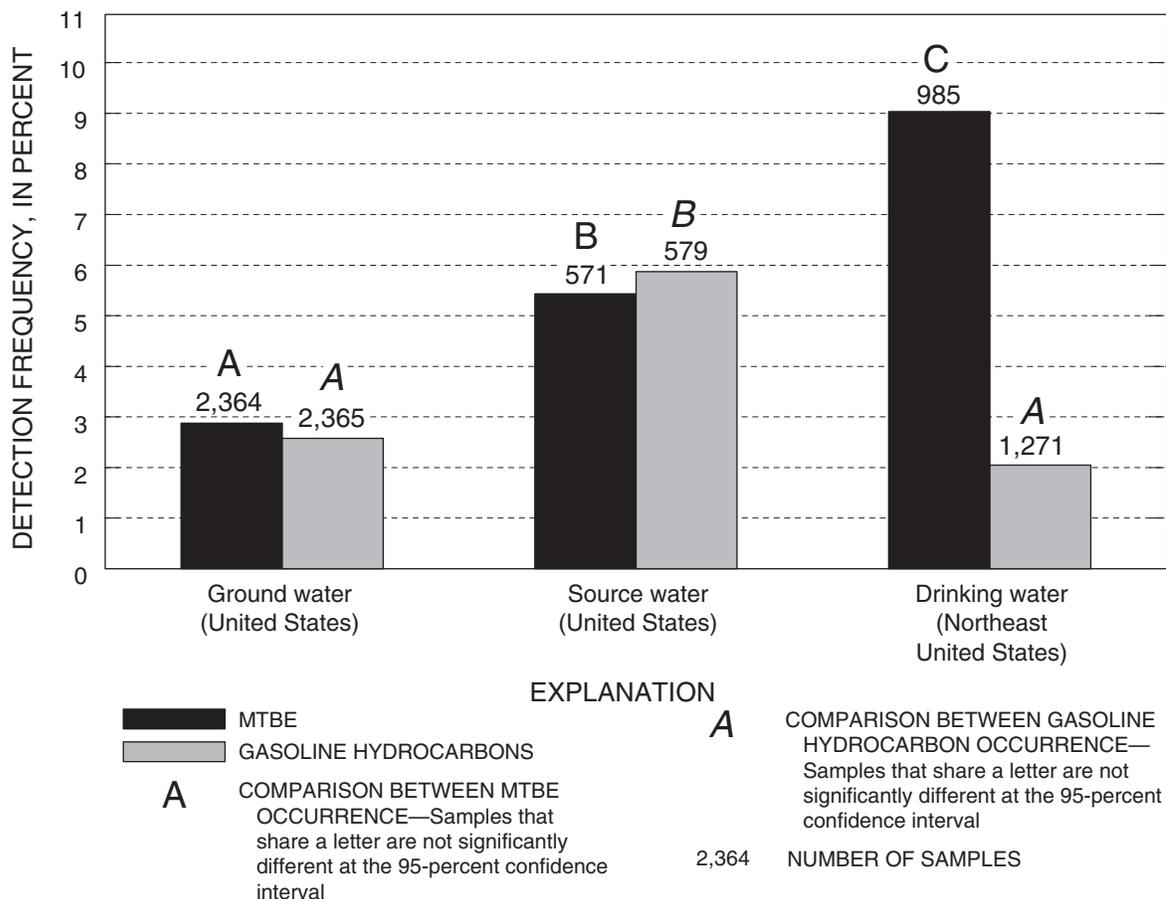


Figure 2. Detection frequencies of MTBE or any gasoline hydrocarbon in samples of ground water, source water and drinking water using an assessment level of 0.2 microgram per liter.

Concentrations

Concentrations of MTBE in each of the three surveys are illustrated in figure 5. In this figure, the data from the ground-water survey include only MTBE concentrations from the major aquifer surveys. An assessment level of 0.2 $\mu\text{g/L}$ was used to make ground-water data comparable to source-water and drinking-water data. However, in ground water many detections of MTBE were below 0.2 $\mu\text{g/L}$. Of all the detections of MTBE in ground water, 38 percent (113 of 300) were less than 0.2 $\mu\text{g/L}$. One reason for the numerous low-level detections in ground water was the information-rich reporting conventions employed by the NWQL for analysis of VOCs in water after 1996. The information-rich method used for analyzing VOCs allows for reporting of concentrations below both the laboratory reporting level and the long-term method detection limit (Oblinger Childress and others, 1999). It has been demonstrated that as the level of detection of a VOC is

lowered, the frequency of detection in ground water increases (Moran, Lapham, and others, 2002).

Similar to detection frequencies, the median detected MTBE concentration was lowest in ground water and highest in drinking water. Using an assessment level of 0.2 $\mu\text{g/L}$, median concentrations were 0.67 $\mu\text{g/L}$ in ground water, 0.71 $\mu\text{g/L}$ in source water, and 1.8 $\mu\text{g/L}$ in drinking water. For ground water, only one sample had a detected concentration above 20 $\mu\text{g/L}$, which is the lower limit of the U.S. Environmental Protection Agency's Drinking-Water Advisory for MTBE (U.S. Environmental Protection Agency, 1997). For source water, no detected MTBE concentration exceeded 20 $\mu\text{g/L}$. For drinking water, nine samples (0.9 percent) had detected MTBE concentrations above 20 $\mu\text{g/L}$. The samples with concentrations of MTBE in drinking water that exceeded 20 $\mu\text{g/L}$ were collected in the following states: Connecticut (2), New York (3), Rhode Island (1), and Virginia (3).

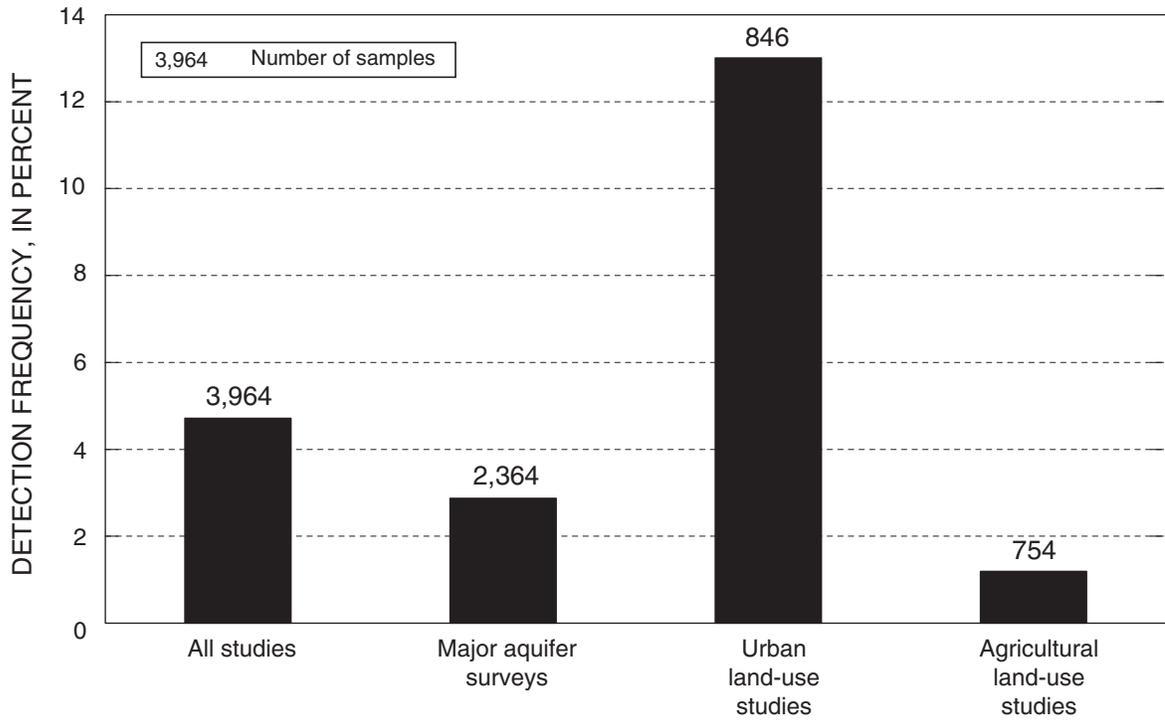


Figure 3. Detection frequencies of MTBE in samples from various NAWQA occurrence studies using no assessment level.

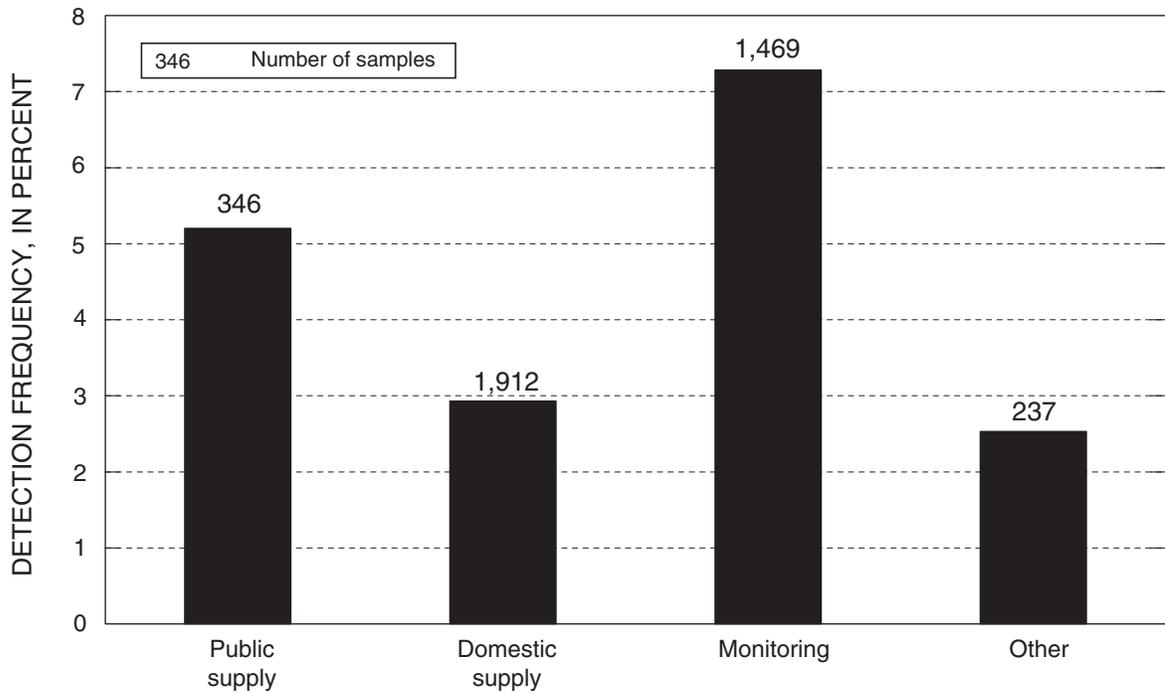
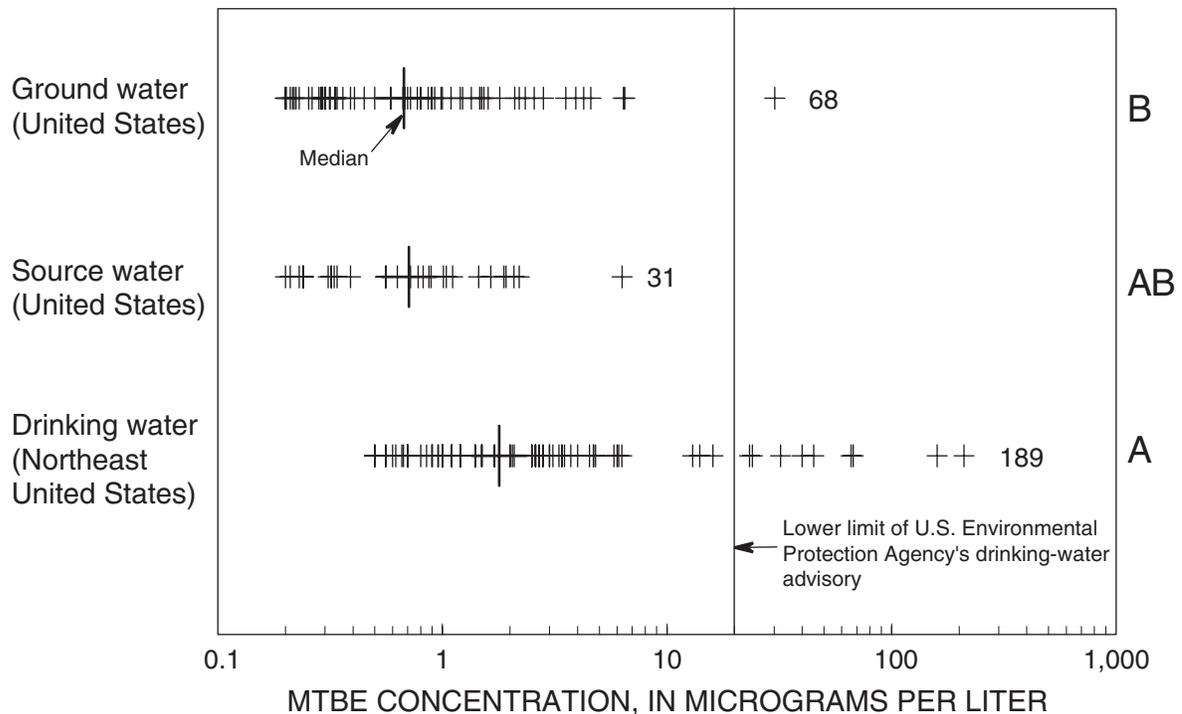


Figure 4. Detection frequencies of MTBE in samples from various well types (NAWQA studies) using no assessment level.



EXPLANATION

A COMPARISON BETWEEN MTBE CONCENTRATIONS—Samples that share a letter are not significantly different at the 95-percent confidence interval

68 NUMBER OF CONCENTRATIONS

Figure 5. MTBE concentrations in samples of ground water, source water, and drinking water using an assessment level of 0.2 microgram per liter. Statistical analyses were performed at an assessment level of 0.5 microgram per liter.

A statistical comparison was made of the MTBE concentrations between each of the three surveys. The statistical analysis was performed at an assessment level of 0.5 µg/L in order to make the data for ground water and source water comparable to the data for drinking water. The results are shown by the letter symbols in figure 5. The results of the statistical analyses indicate that the distributions of MTBE concentrations between ground water and drinking water were significantly different ($p < 0.05$), but the distributions of MTBE concentrations between ground water and source water and between source water and drinking water were not significantly different ($p > 0.05$). Quantile-quantile plots indicated that the concentrations of MTBE in drinking water were higher than the concentrations of MTBE in either ground water or source water.

Gasoline Hydrocarbons

The detection frequency of one or more gasoline hydrocarbons in each of the three data sets also is illustrated in figure 2. Data for ground water and source water were analyzed at an assessment level of 0.2 µg/L to make them comparable to data for drinking water. For ground-water data, the detection frequency is only for gasoline hydrocarbon analyses in the major aquifer surveys. The bold italic letters in figure 2 graphically display the results of chi-square tests of independence comparing the detection frequencies of gasoline hydrocarbons between the three surveys.

The detection frequency of one or more gasoline hydrocarbons was lowest in drinking water and highest in source water (fig. 2). For ground water and drinking water, the detection frequency of one or more gasoline

hydrocarbons was less than the detection frequency of MTBE. However, the detection frequency of one or more gasoline hydrocarbons in source water was slightly higher than the detection frequency of MTBE (fig. 2). The detection frequencies of one or more gasoline hydrocarbons were not dependent on the survey between ground water and drinking water ($p > 0.05$) but were dependent on the survey between source water and ground water and between source water and drinking water ($p < 0.05$).

Individually, gasoline hydrocarbons were detected less frequently than MTBE in all three surveys. In source water, the detection frequencies of individual gasoline hydrocarbons were highest. However, individual gasoline hydrocarbons were detected in less than 4 percent of source-water samples, with toluene being detected most frequently in 3.5 percent of samples. In ground water and drinking water, the detection frequencies of any individual gasoline hydrocarbon were even less, with no compound found in more than 2 percent and 1 percent of samples. Like source water, the most frequently detected gasoline hydrocarbon in ground water and drinking water was toluene detected in 1 percent of samples and in 0.6 percent of samples.

Benzene

An important aspect of the RFG Program is the limitation of benzene in reformulated gasoline to less than or equal to 1 percent by volume (U.S. Environmental Protection Agency, 1990). Normally gasoline contains between 1 and 1.5 percent benzene by volume. Although gasoline in the Oxyfuel Program areas is not required to have a 1-percent benzene limitation, the high content of MTBE required by the Oxyfuel Program (15 percent by volume) probably results in the displacement of other fuel components such as benzene. This means that gasoline in areas of high MTBE use should contain less benzene relative to areas of low MTBE use, and detection frequencies and concentrations of benzene should be lower in areas of high MTBE use relative to areas of low MTBE use.

An examination of data from ground water indicated that the detection frequency of benzene was higher in areas of low MTBE use, at 4.7 percent, relative to the detection frequency of benzene in areas of high MTBE use, at 2 percent, when no assessment level was applied. The detection frequency of benzene also was dependent on MTBE use ($p < 0.05$) but the distributions of concentrations of benzene were not

significantly different between areas of high and low MTBE use ($p > 0.05$).

Other Ethers

In addition to MTBE, the NAWQA Program analyzed for three other alkyl ethers that have been used commercially as gasoline oxygenates (Zogorski and others, 1997). These ethers have been used to a more limited extent as gasoline oxygenates compared to MTBE, and they generally are not used in conjunction with MTBE but as substitutes. These compounds were analyzed in both the NAWQA ground-water survey and the source-water survey and include *tert*-amyl methyl ether (TAME), diisopropyl ether (DIPE), and ethyl *tert*-butyl ether (ETBE). In ground water at an assessment level of 0.2 $\mu\text{g/L}$, only two of the three ethers were detected—TAME and DIPE. The detection frequencies of both of these compounds were less than MTBE and they were detected in less than 1 percent of samples. TAME was detected in 0.25 percent of samples (6 of 2,382 samples), whereas DIPE was detected in 0.19 percent of samples (4 of 2,077 samples). The fewer number of ground-water samples that were analyzed for ethers as compared to MTBE resulted from these compounds not being analyzed by the NWQL until April 1996, when they were added to the analytical method.

In source water, all three ethers were detected at least once at an assessment level of 0.2 $\mu\text{g/L}$. Like ground water, the detection of any of these ether compounds in source water was considerably less than the detection of MTBE. Both TAME and DIPE were detected in only 0.3 percent of source-water samples (2 of 579 samples), whereas ETBE was detected in only one sample. No analyses of other ether oxygenates were available for data from the drinking-water survey.

Factors Affecting Occurrence

A variety of hydrogeologic and anthropogenic factors are responsible for the occurrence and concentrations of MTBE in ground water. Identifying the sources and basic transport mechanisms of MTBE is vital in understanding its occurrence and the associated potential exposure risks. Using various statistical techniques, it is possible to identify anthropogenic and

hydrogeologic variables that are related to the occurrence of MTBE in ground water. By identifying anthropogenic variables, like MTBE use and land use that are related to the occurrence of MTBE, it is possible to make inferences about potential sources. By identifying hydrogeologic variables, like recharge and soil permeability that are related to the occurrence of MTBE, it is possible to make inferences about the transport mechanisms and fate of MTBE in ground water and the vulnerability of various aquifers to MTBE contamination.

Sources of MTBE

Most of the MTBE used in the United States is for oxygenation of gasoline. Thus, the primary source of most MTBE in the environment is assumed to be gasoline. Besides gasoline, used motor lubricating oil, home heating oil, and diesel fuel also have been identified as containing MTBE because of mixing with gasoline that contains MTBE (Robbins and others, 1999, 2000; Baker and others, 2002). Releases of these products also could be possible sources of MTBE. Some potential non-point sources of MTBE include evaporative losses from tanks or pipelines, incomplete combustion in engines, urban storm-water runoff from areas with small spills, exhaust from motorized watercraft with incomplete combustion, and leaks from watercraft tanks. Some potential point sources of MTBE to the environment include leaks from large domestic or commercial gasoline, diesel fuel, heating oil, or waste oil storage tanks and associated piping (underground and aboveground), leaks from transport pipelines or bulk stations, motor vehicle or truck accidents, overfill spills, and large consumer releases.

In this report, non-point sources are identified as widespread and diffuse releases of MTBE and gasoline hydrocarbons leading to relatively low concentrations in ground water. Point sources are identified as intense sources of MTBE and gasoline hydrocarbons leading to relatively high concentrations in ground water. Although this is assumed, point sources can lead to low concentrations of MTBE and gasoline hydrocarbons by dilution and dispersion during advective transport.

Very few samples analyzed in the three surveys had concentrations of MTBE greater than 20 µg/L. It is believed that MTBE concentrations greater than 20 µg/L in ground water are the result of point source releases (Moran and others, 1999). It would be unlikely for non-point sources to cause higher concentrations in

ground water than this level. Certain intense non-point sources of MTBE, such as atmospheric concentrations around certain parking garages, gas stations, or roadways, could result in MTBE concentrations of as much as 20 µg/L in shallow ground water through atmospheric deposition (Squillace and others, 1997). However, unless there is some concentrating mechanism, such as bioconcentration by plants, the concentration of MTBE from a purely atmospheric source can never exceed the equilibrium water concentration without the addition of other sources. Therefore, if the concentration of MTBE is greater than the highest likely type of non-point source, the source must be a point source. Low concentrations of MTBE, on the other hand, could have either point or non-point sources.

In general, the occurrence of gasoline hydrocarbons with MTBE in a ground-water sample suggests proximity to a gasoline release. However, MTBE did not occur frequently with gasoline hydrocarbons in the three surveys. In all data sets combined and at an assessment level of 0.2 µg/L, MTBE occurred in a total of 307 samples and gasoline hydrocarbons occurred together with MTBE in only 28 of these samples (9 percent). However, when MTBE concentrations were divided into categories reflecting relatively low, medium, and high concentrations, a pattern in the occurrence of gasoline hydrocarbons and MTBE together became apparent (fig. 6). For relatively low (less than 1 µg/L) and medium (1 µg/L to less than 20 µg/L) concentrations of MTBE, the occurrence of gasoline hydrocarbons at an assessment level of 0.2 µg/L was less than 10 percent. However, for relatively high (greater than 20 µg/L) MTBE concentrations, the occurrence of any gasoline hydrocarbon was substantially higher at 41 percent (fig. 6). Although the number of samples represented by high MTBE concentrations in figure 6 is small relative to the other two categories, the trend in the data is quite clear. As concentrations of MTBE increase, the occurrence of gasoline hydrocarbons with MTBE increases. This indicates that samples with higher concentrations of MTBE are located in proximity to gasoline releases relative to samples with lower concentrations of MTBE.

Use of MTBE in Gasoline as a Surrogate for Environmental Input

To understand the occurrence of MTBE in the environment, it would be ideal to know the exact

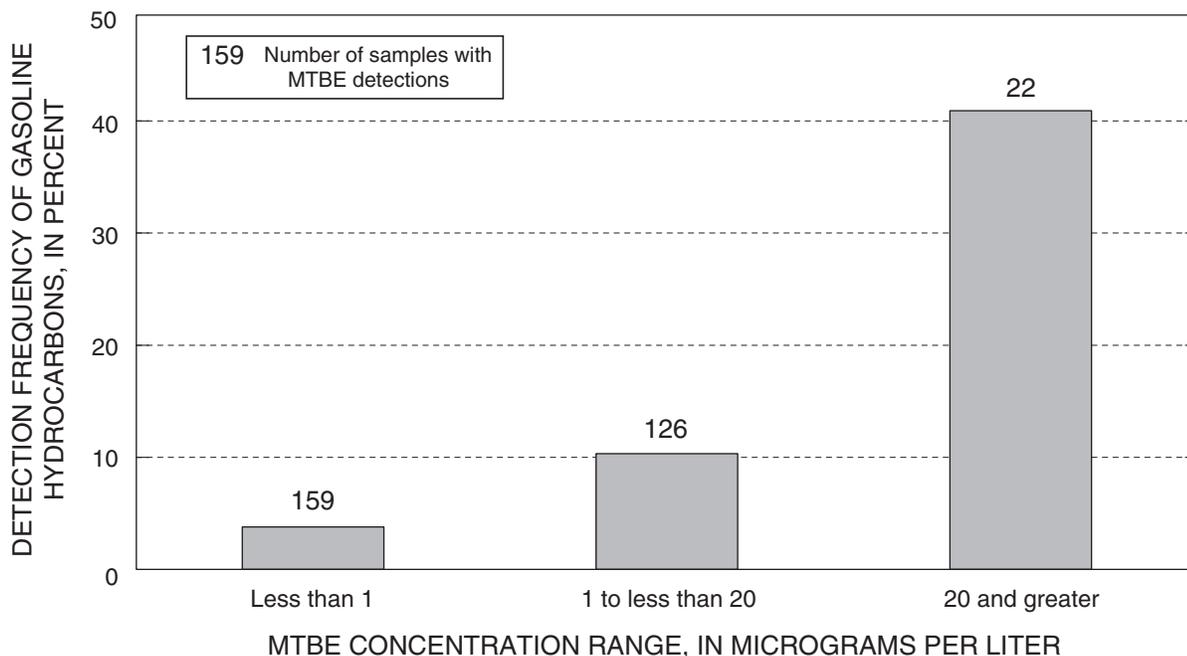


Figure 6. Detection frequencies of any gasoline hydrocarbon in samples of ground water for selected concentration ranges of MTBE using an assessment level of 0.2 microgram per liter.

location and amount of all releases of MTBE to the environment. At a national scale, such knowledge is impossible to identify or ascertain. However, because almost all MTBE is used in gasoline, releases of MTBE to the environment should be related to the amount of MTBE used in gasoline. Use of MTBE in gasoline in various areas of the country can be estimated in several ways. One way of estimating use is by considering areas previously or currently under the RFG Program and where MTBE is used as the gasoline oxygenate as being areas where high amounts of MTBE are used.

Further refinement and specificity in determining MTBE use can be obtained using information from gasoline surveys. Several surveys have been conducted to provide information on the physical properties and constituents of gasoline including octane number, specific gravity, and volumes of olefins, aromatics, benzene, alcohols, and various ether oxygenates. The surveys provide information on MTBE content in gasoline, in percent by volume, for areas that are included within the surveys. The purposes of these surveys are to provide comparative information on gasoline composition to companies interested in the physical and chemical properties of fuels and to verify that oxygen content in gasoline is sufficient to meet RFG and Oxyfuel

Program requirements. Additional information on these surveys can be found in Moran, Clawges, and Zogorski (2002).

Samples from the three surveys were placed into two groups based on the following categorization scheme: (1) relatively high MTBE use, and (2) relatively low MTBE use or unknown MTBE use. A sample was designated as being from an area of relatively high MTBE use if either: (1) the sample was located in an area that was designated for RFG usage at any time from 1993-2001 and where MTBE was used as the gasoline oxygenate, or (2) the sample was located in an area where gasoline surveys indicated a long-term average for MTBE content in gasoline, from 1990-99, of greater than or equal to 3 percent by volume. If either 1 or 2 were not true for a sample, or if the MTBE use in the area where the sample was located was unknown, the sample was coded as being from an area of relatively low MTBE use. Using this categorization scheme, each sample was placed into a category of high or low MTBE use.

Detection frequencies of MTBE within areas of high and low MTBE use for each survey are presented in figure 7. Data for ground water and source water were analyzed at an assessment level of 0.2 µg/L to

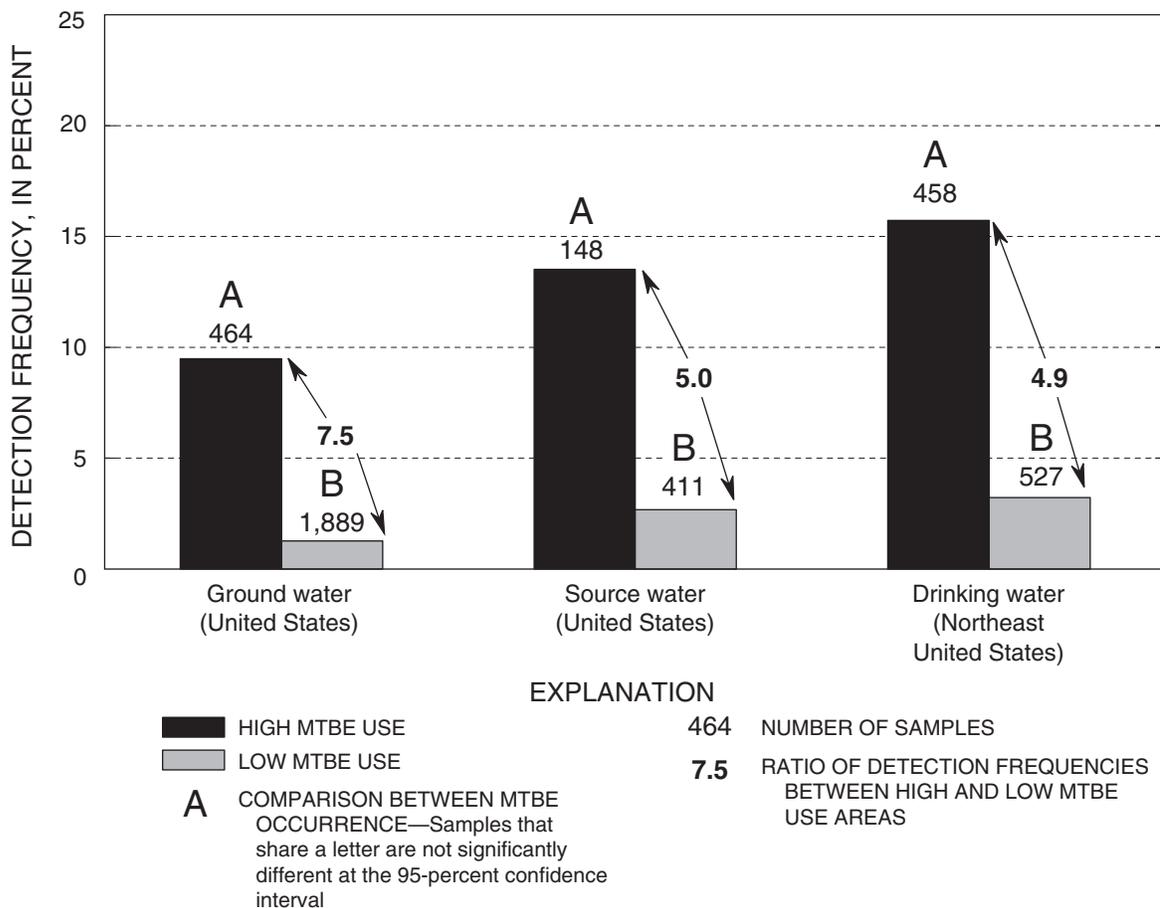


Figure 7. Detection frequencies of MTBE in samples of ground water, source water, and drinking water for areas of high and low MTBE use using an assessment level of 0.2 microgram per liter.

make them comparable to data for drinking water. For ground-water data, the detection frequency is only for MTBE analyses in the major aquifer surveys. The letters above each bar represent the results of chi-square tests of independence for each survey between areas of high and low MTBE use. The numbers between the arrows represent the ratios of detection frequencies between areas of high and low MTBE use.

For each survey the detection frequency of MTBE was higher in areas of high MTBE use compared to areas of low MTBE use. For each survey, the detection frequencies of MTBE were dependent on MTBE use ($p < 0.05$). The ratios of detection frequencies between areas of high and low MTBE use varied from 4.9 for drinking water to 7.5 for ground water. This indicates that the detection frequency of MTBE was about 5 to 7.5 times higher in areas of relatively high MTBE use compared to areas of relatively low

MTBE use. When comparing between the surveys in areas of either high or low MTBE use, the detection frequencies of MTBE also were dependent on the survey ($p < 0.05$).

Research has shown that the probability of detecting MTBE at or above 0.5 $\mu\text{g/L}$ in ground water is related to population density (Squillace and Moran, 2000). An analysis was performed to determine if the detection frequency of MTBE is related to population density. In order to control for MTBE use, a comparison was made of the detection frequencies of MTBE between areas of high and low population density for areas of high and low MTBE use. For this analysis, only data from ground water were used because the data for source water had too few detections to provide a meaningful comparison and the data for drinking water were too limited in geographic extent to provide a good overall national distribution. Population density

is related to areas of urban and non-urban land use. Areas with population densities less than 50 people/km² (square kilometer) can be classified as non-urban, whereas areas with population densities greater than 50 people/km² can be classified as urban (Hitt, 1994). This population density classification scheme was used to place all samples within a land-use category of either urban or non-urban.

Detection frequencies of MTBE in ground water between urban and non-urban land-use areas and areas of high and low MTBE use are presented in figure 8. In this analysis, ground-water data from all NAWQA occurrence studies were used. No assessment level was applied in determining detection frequency in ground water in figure 8 because no comparisons were made to other data sets. The numbers between the arrows represent the ratios of detection frequencies between urban and non-urban areas. When controlling for MTBE use, the detection frequency of MTBE in ground water was

clearly related to population density (fig. 8). The ratios of detection frequencies between urban and non-urban land-use areas for high and low MTBE use were 3 and 5. The ratios of detection frequencies between MTBE use areas were higher than the ratios of detection frequencies between land-use areas. This suggests that, although population density is an important factor affecting the occurrence of MTBE, MTBE use in gasoline may be more important.

A comparison was made of the concentrations of MTBE in ground water between areas of high and low MTBE use. In order to make the comparison equitable, the effect of population density on MTBE concentrations was considered. Based on the previous analyses, only samples with a population density of greater than or equal to 50 people/km² were selected. Thus, a comparison of the concentrations of MTBE in urban land-use areas for areas of high and low MTBE use was made. Figure 9 is a quantile-quantile plot of MTBE

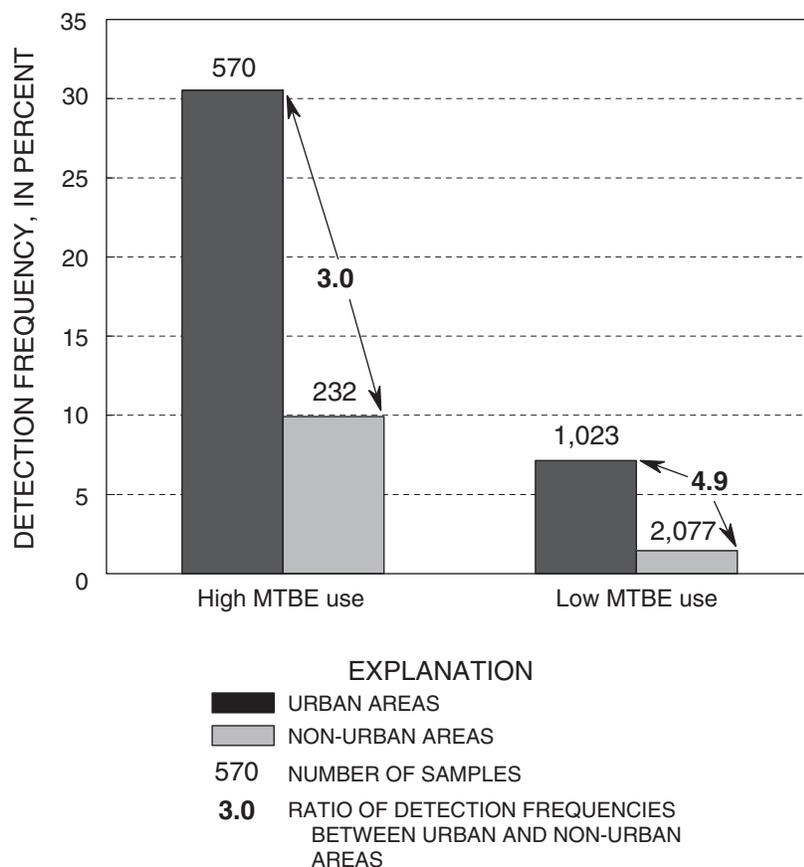


Figure 8. Detection frequencies of MTBE in samples of ground water for areas of urban and non-urban land use and by areas of high and low MTBE use using no assessment level.

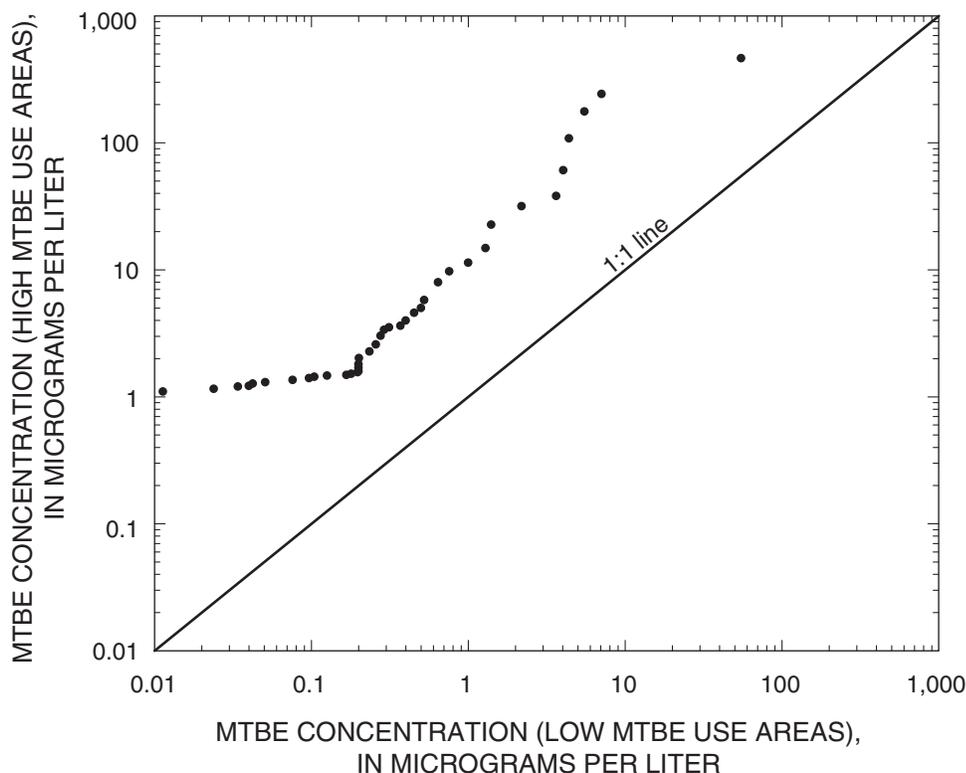


Figure 9. Comparison of the distributions of concentrations of MTBE in ground water in areas of urban land use for areas of high and low MTBE use using no assessment level.

concentrations in ground water for urban land-use areas and between areas of high and low MTBE use. Because the data are solely for ground water, no assessment level was applied. Each point in figure 9 represents the MTBE concentration corresponding to the same quantile in each data set. The quantiles computed for plotting ranged from 0.01 to 1.0, in increments of 0.01. For simplicity, the quantile pairs of non-detections are not plotted in figure 9. All data pairs are above the 1:1 line indicating that higher concentrations of MTBE occur in areas of high MTBE use relative to areas of low MTBE use (fig. 9). A statistical test indicated that the distributions of MTBE concentrations were significantly different between areas of high and low MTBE use ($p < 0.05$).

MTBE and Dissolved Oxygen in Ground Water

An analysis of MTBE occurrence under oxic and anoxic ground-water conditions was performed. Oxic ground water is defined in this report as ground water that contains greater than 0.5 mg/L (milligrams per liter) of dissolved oxygen, whereas anoxic ground

water is defined as ground water that contains less than or equal to 0.5 mg/L of dissolved oxygen. Freeze and Cherry (1979) indicated that natural ground water is considered oxidized if it has a redox potential (pE) value above 13.4, which is approximately equal to a dissolved-oxygen value of 0.5 mg/L. In this report, only samples of ground water were used because dissolved-oxygen information was not available for either source-water or drinking-water data. In order to control for MTBE use, only samples from high MTBE use areas were examined.

When no assessment level was applied, the detection frequency of MTBE in oxic ground water was similar at 24.5 percent to the detection frequency of MTBE in anoxic ground water at 22.5 percent, and the detection frequencies of MTBE were not dependent on dissolved-oxygen conditions ($p > 0.05$). An analysis of MTBE concentrations and dissolved oxygen, both as continuous variables and using no assessment level, indicated that there was not a monotonic relation between the two variables ($p > 0.05$).

However, when only higher concentrations of MTBE were considered by applying various assessment levels to the data, the detection frequencies of MTBE in oxic and anoxic ground water were different. When an assessment level of 0.2 µg/L was applied to MTBE concentrations, the detection frequency of MTBE in oxic ground water was 14.1 percent, and the detection frequency of MTBE in anoxic ground water was 18.3 percent; however, the detection frequencies of MTBE were not dependent on dissolved-oxygen conditions ($p > 0.05$). When an assessment level of 0.5 µg/L was applied to MTBE concentrations, the detection frequency of MTBE in oxic ground water was 7.6 percent, and the detection frequency of MTBE in anoxic ground water was 14.8 percent. In this case, the detection frequencies of MTBE were dependent on dissolved-oxygen conditions ($p < 0.05$). When an assessment level of 0.5 µg/L was applied to MTBE concentrations, a significant monotonic relation was found between MTBE concentrations and dissolved-oxygen concentrations, with the concentration of dissolved oxygen decreasing as the concentration of MTBE increased (Spearman rho = -0.119; $p < 0.05$).

Other Associations with MTBE in Ground Water

Associations between MTBE occurrence and various hydrogeologic and anthropogenic variables were examined using multivariate logistic regression. For the logistic regression analyses, only data from ground water were used because hydrogeologic and anthropogenic information was scarce or not available for the source-water and drinking-water surveys. The dependent or response variable was the detection of MTBE, and no assessment level was applied to the MTBE data because no comparison was made to other data sets. Table 1 lists the explanatory variables that were used for these analyses, the units for each variable, the coding of the variable in the logistic regression analyses, and the source of the data. Prior to analysis, population density was transformed using a natural logarithm function to normalize the distribution.

Table 2 summarizes the results of the logistic regression analyses for the explanatory variables that were significantly associated with MTBE occurrence, including the standardized estimated slope coefficients. The magnitude and sign of the slope coefficients deter-

mines the strength and direction of the association of the probability of detecting MTBE with the explanatory variables according to the following equation:

$$P = \frac{e^{(\beta_0 + \beta_1 X_1 + \dots + \beta_i X_i)}}{1 + e^{(\beta_0 + \beta_1 X_1 + \dots + \beta_i X_i)}}$$

where

- P = probability of detecting MTBE,
- β_0 = y-intercept,
- β_i = slope coefficient of X_i explanatory variables, and
- $X_i = 1$ to i explanatory variables.

Estimated slope coefficients with positive signs indicate an increase in the probability of detecting MTBE with an increase in the explanatory variable, whereas estimated slope coefficients with negative signs indicate a decrease in the probability of detecting MTBE with an increase in the explanatory variable. However, estimated coefficients do not give an accurate assessment of the strength of the association because the units of each variable, especially continuous variables, have large differences in magnitude and variance. Therefore, standardized slope coefficients were computed in order to compare the coefficients directly between one another (table 2). The standardized coefficients indicate how many standard deviations of change in the dependent variable are associated with one standard deviation of change in the explanatory variable (Menard, 2002).

Based on a step-wise modeling approach, the explanatory variables found to be significantly associated with the probability of detecting MTBE in ground water included population density, use of MTBE in gasoline, recharge, aquifer consolidation, soil permeability, and the density of leaking underground gasoline storage tanks (table 2). Population density, use of MTBE in gasoline, and the density of leaking underground gasoline storage tanks in the vicinity of the sampled well represent anthropogenic influences that help to approximate input of MTBE to the environment.

Table 1. Anthropogenic and hydrogeologic variables that were used in the logistic regression analysis[GWSI, U.S. Geological Survey Ground Water Site Inventory database; km², square kilometers; m, meters]

Explanatory variable	Units	Coding	Source
Anthropogenic Variables			
Use of MTBE in gasoline	None	Binary (0, low MTBE use; 1, high MTBE use)	U.S. Environmental Protection Agency, 2003c; TRW Petroleum Technologies, written commun., 1999
Population density	People/km ² (interpolated)	Continuous	U.S. Census Bureau, 2001
Urban land-use	Percent within 500-m buffer	Continuous	Vogelmann and others, 2001
Aboveground storage tanks	Tanks/500-m grid cell (interpolated)	Continuous	C.V. Price, U.S. Geological Survey, written commun., 2003
Underground storage tanks	Tanks/500-m grid cell interpolated)	Continuous	C.V. Price, U.S. Geological Survey, written commun., 2003
Leaking underground storage tanks	Tanks/500-m grid cell (interpolated)	Continuous	C.V. Price, U.S. Geological Survey, written commun., 2003
Hydrogeologic Variables			
Well depth	Feet	Continuous	GWSI
Depth to the top of the screened interval	Feet	Continuous	GWSI
Water level	Feet below land surface datum	Continuous	GWSI
Land surface slope	Percent	Continuous	U.S. Department of Agriculture, 1994
Depth to seasonal high water table in soil	Inches	Continuous	U.S. Department of Agriculture, 1994
Soil permeability	Inches/hour	Continuous	U.S. Department of Agriculture, 1994
Soil organic matter content	Percent by weight	Continuous	U.S. Department of Agriculture, 1994
Soil clay content	Percent	Continuous	U.S. Department of Agriculture, 1994
Aquifer confinement	None	Categorical	GWSI
Aquifer consolidation	None	Binary (0, consolidated; 1, unconsolidated)	GWSI
Recharge	Millimeters per year	Continuous	D.M. Wolock, U.S. Geological Survey, written commun., 2003

Population density was the anthropogenic variable that was found to be most strongly associated with the probability of detecting MTBE as indicated by the standardized coefficient for population density in table 2. This means that an increase in population density results in the greatest increase in the probability of detecting MTBE when controlling for the other significant explanatory variables. Use of MTBE in gasoline also was strongly associated with the probability of detecting MTBE. When controlling for the other significant explanatory variables, the probability of detecting MTBE was about 5.8 times higher in high MTBE use areas compared to low MTBE use areas.

Although the density of leaking underground gasoline storage tanks in the vicinity of the sampled well also was associated with the probability of detecting MTBE in ground water, the effect of this variable on the probability of occurrence was much smaller relative to population density and use of MTBE in gasoline (table 2).

The other variables significantly associated with the probability of detecting MTBE in ground water included recharge, aquifer consolidation, and soil permeability (table 2). These variables represent hydrogeologic conditions that affect the transport and fate of MTBE in the environment. Recharge was the hydrogeologic variable found to be most strongly associated

with the probability of detecting MTBE in ground water. The probability of detecting MTBE in ground water increased as recharge increased. Although aquifer consolidation and soil permeability also were associated with the probability of detecting MTBE in ground water, the effect of these variables on the probability of occurrence was much smaller relative to recharge. The probability of detecting MTBE in ground water was higher in aquifers composed of consolidated material compared to aquifers composed of unconsolidated material. As soil permeability increased, the probability of detecting MTBE in ground water also increased.

IMPLICATIONS INVOLVING MTBE AND GASOLINE HYDROCARBONS

The overall detection frequency of MTBE for all three surveys combined was less than 10 percent using no assessment level. This means that less than 1 of 10 samples had a detectable concentration of MTBE. One explanation for this relatively low national detection frequency may be that large quantities of MTBE have been used only relatively recently in oxygenated gasoline and the use of oxygenated gasoline has been highly regionalized. Drinking water in the Northeast region of the country had the highest frequency of MTBE detections among the three surveys. This region is an area of substantial current and former use of oxygenated gasoline, has a long-term history of dense urbanization and high population, and may be an area of greater aquifer vulnerability.

Table 2. Anthropogenic and hydrogeologic variables that were significantly associated with the probability of detecting MTBE in ground water

Explanatory variable	Estimated coefficient	Standardized slope coefficient
Anthropogenic Variables		
Population density	0.367	2.4
Use of MTBE in gasoline	1.765	2.1
Leaking underground storage tanks	0.463	.04
Hydrogeologic Variables		
Recharge	0.005	.17
Aquifer consolidation	-0.582	-.08
Soil permeability	0.043	.05

The overall detection frequency of MTBE for all three surveys, at 7.6 percent, was higher than the detection frequency of trichloroethene (4.5 percent) but lower than the detection frequency of tetrachloroethene (11.9 percent). Both trichloroethene (TCE) and tetrachloroethene (PCE) have much longer production histories than MTBE and both have been produced and used in the United States since 1923 (Pankow and Cherry, 1996). MTBE has only been produced substantially since about 1970, although production of MTBE in the United States has outpaced both TCE and PCE since about 1980 (Johnson and others, 2000). Consequently, it is surprising to find the detection frequency of MTBE rivaling or surpassing these VOCs that have been produced and used for much longer periods of time. This indicates that MTBE contamination is an important concern with respect to ground-water management.

MTBE in Drinking Water

The detection frequency of MTBE was higher in drinking water in the Northeast compared to the national surveys of source water or ground water. The higher detection frequency of MTBE in drinking water may be related to: (1) the data on drinking water are only for public-supply wells, which generally have large pumping capacities; (2) the detection frequencies in drinking water may be biased high because the Northeast and Mid-Atlantic regions are areas of high MTBE use; and (3) the data on drinking water did not reflect occurrence by specific source but instead was summarized by system.

Because the drinking-water data were exclusively from public-supply wells, a higher detection frequency of MTBE might be expected as public-supply wells generally have higher pumping rates and larger areas contributing recharge to the well than other well types such as private-supply wells (domestic) and monitoring wells (Moran, Lapham, and others, 2002). Stackelberg and others (2000) found that the number and total concentrations of VOCs per sample were significantly higher in ground water from public-supply wells compared to monitoring wells in the surficial Kirkwood-Cohansey aquifer system in southern New Jersey. The larger volumes of water withdrawn from public-supply wells compared to monitoring wells and the subsequently larger contributing areas were believed to be responsible for intercepting more ground water flowing from

VOC point sources (Stackelberg and others, 2000). Bruce and Oelsner (2001) found that closely located domestic and public-supply wells did not have similar detection frequency of pesticides and public-supply wells had a higher detection frequency of pesticides. They attributed the higher detection frequency of pesticides in public-supply wells to the higher pumping rate and seasonal pumping cycles of these wells that produced more recently recharged water containing more anthropogenic compounds.

Another factor that may have contributed to a higher detection frequency of MTBE in public-supply wells is their location in the Northeast and Mid-Atlantic regions where substantial use of oxygenated gasoline has occurred and where MTBE was the primary oxygenate. In areas of substantial use of MTBE in gasoline, an increased probability of release of MTBE to the environment and transport to ground water exists.

Finally, the data on MTBE in drinking water were summarized by system and this may have resulted in a bias towards a higher detection frequency because many systems had multiple sources with multiple samples (Grady and Casey, 2001). In fact, when the detection frequency of MTBE for drinking water was computed for both ground-water and surface-water sources relative to the number of samples, rather than the number of systems, it was lower at 6.2 percent compared to 9 percent when summarized by system (Grady and Casey, 2001).

When the data for ground water and source water were limited in extent to only the 12 Northeast and Mid-Atlantic States and an assessment level of 0.5 µg/L was applied, the detection frequencies of MTBE in ground water and source water were comparable to the detection frequency of MTBE in drinking water. This indicates that the occurrence of MTBE in ground water, source water, and drinking water is similar when controlling for use of MTBE.

MTBE Occurrence by Land Use and Well Type

For ground water, the detection frequency of MTBE was highest in the NAWQA urban land-use studies compared to the major aquifer surveys or agricultural land-use studies. The higher detection frequency of MTBE in urban land-use studies probably is a result of several factors: (1) these are areas of highest population density and thus highest gasoline use, (2) highly urban regions like the Northeast and parts of

California have most intense use of MTBE in gasoline, and (3) the NAWQA urban land-use studies targeted shallow ground water and were designed to sample recently recharged ground water generally less than 10 years old. Thus, shallow ground water underlying urban land-use areas is at greater risk of contamination by MTBE than ground water underlying rural land-use areas. However, it is not known if contamination of shallow ground water will reach deeper aquifers used for supplying drinking water.

For ground water, the detection frequency of MTBE was highest in monitoring wells compared to other well types. The higher detection frequency of MTBE in monitoring wells is due to several factors: (1) monitoring wells were used extensively in the urban land-use studies, and (2) many monitoring wells were installed by NAWQA for land-use studies and were shallow in depth, designed to sample recently recharged ground water near the top of the water table. Although NAWQA sampled fewer public-supply wells compared to domestic wells, the detection frequency of MTBE in public-supply wells was higher. As previously mentioned, the detection frequency of many VOCs has been shown to be higher in public-supply wells compared to domestic wells for several reasons. Because public water-supply systems that use ground water as a source of drinking water served over 100 million people as of 2001 (Harrigan-Farrelly, 2002), the potential of human exposure to MTBE from ground-water contamination is large.

MTBE Concentrations and Human Health

The median detected MTBE concentration in ground water and source water was less than 1 µg/L, and the median detected MTBE concentration in drinking water was less than 2 µg/L. These relatively low concentrations indicate that many of the MTBE detections could be from non-point sources or that point sources have not caused widespread areas of high-level concentrations near the samples.

High concentrations of MTBE (>20 µg/L) are believed to result from point sources of contamination; however, the NAWQA Program sampling does not allow for definitive identification of sources of MTBE. When the concentration of MTBE was considered, the occurrence of any gasoline hydrocarbon together with MTBE was substantially increased for higher concentrations of MTBE. This indicates that

ground-water samples with higher concentrations of MTBE are located in proximity to gasoline releases relative to samples with lower concentrations of MTBE. Low concentrations of MTBE (<20 µg/L) probably are the result of an unknown mix of point and non-point sources. Additional research is needed to better understand the sources of low concentrations of MTBE.

No samples of source water exceeded the lower limit of the U.S. Environmental Protection Agency's Drinking-Water Advisory. The incidence of MTBE concentrations exceeding the lower limit of the advisory relative to all samples was quite low for both ground water and drinking water. Thus, most of the ground water and drinking water analyzed in this report did not contain MTBE concentrations that would cause organoleptic effects.

However, the potential long-term human health effects of low-level concentrations of MTBE in drinking water are not well understood, and there have been different conclusions drawn from the relatively few animal studies that have been done (Toccalino, 2003). Intake of MTBE by gavage has been associated with acute and long-term (carcinogenic) health effects in laboratory animals, and the validity of some of the interpretations drawn from these studies has been questioned (Robinson and others, 1990; Belpoggi and others, 1995). In 1997, the U.S. Environmental Protection Agency issued a drinking-water advisory recommending that MTBE concentrations in drinking water be below the range of 20 to 40 µg/L to protect consumer acceptance (taste and odor) and also to provide a large margin of safety from toxic effects (U.S. Environmental Protection Agency, 1997). The U.S. Environmental Protection Agency is continuing to assess the human health effects of MTBE and the implications of setting a drinking-water standard (Davis, 2002). To be protective of carcinogenic potential and reproductive and developmental effects, maximum levels of MTBE in drinking water ranging from 5 to 100 µg/L have been suggested by other agencies and individuals (Johnson, 1998; Hartley and others, 1999). The California Department of Health Services has issued a Maximum Contaminant Level for MTBE in drinking water of 13 µg/L (California Department of Health Services, 2002). Considering the current level of concern regarding the health effects of MTBE and the continuing uncertainty of the health effects of MTBE, monitoring of drinking water for MTBE is still needed.

Gasoline Hydrocarbon Occurrence

For ground water and drinking water, the detection frequencies of one or more gasoline hydrocarbons or individual gasoline hydrocarbons were less than the detection frequency of MTBE. The lower detection frequencies of gasoline hydrocarbons compared to MTBE are believed to be a result of differences in transport and fate properties between the different compounds. MTBE has higher water solubility than gasoline hydrocarbons. MTBE adsorbs only weakly to subsurface solids, whereas gasoline hydrocarbons adsorb relatively strongly. As a result, MTBE moves at velocities that are similar to the velocities of local ground water, whereas the velocities of gasoline hydrocarbons are retarded relative to the velocities of local ground water (Squillace and others, 1997). In addition, the aerobic half-life of MTBE in ground water has been estimated to be approximately an order of magnitude longer than the average aerobic half-life of most gasoline hydrocarbons in ground water (Howard and others, 1991). Aerobic half-lives in ground water were selected for comparison because approximately 70 percent of NAWQA ground-water samples had sufficient dissolved oxygen (>0.5 mg/L) to be classified as oxic. Finally, the percent volume of MTBE in oxygenated gasoline is generally higher than the percent volume of the gasoline hydrocarbons examined in this report (Canadian Petroleum Products Institute, 1994). All of the above properties make it more likely that MTBE will be detected in ground water if released to the environment compared to gasoline compared to gasoline hydrocarbons.

The limitation of benzene content in gasoline in the RFG Program may have resulted in lower detection frequencies of benzene in ground water in areas of high MTBE use relative to areas of low MTBE use, but has not resulted in lower benzene concentrations. The lower detection frequencies of benzene in ground water in these areas probably also are reflected in source water and drinking water. Because benzene is a known human carcinogen (U.S. Environmental Protection Agency, 2000), the lower detection frequencies are a significant change in improving ground-water quality and would be particularly important for drinking-water sources. However, at present (2003) the data for source water and drinking water do not yield similar findings, which indicates that the influence of the RFG Program on the environmental occurrence of benzene is not completely understood and that more research in this area is warranted.

Associations with MTBE Occurrence

When use of MTBE in gasoline was used as surrogate for input of MTBE to the environment, there was a significant difference in the detection frequency of MTBE between areas of high and low MTBE use. The detection frequency of MTBE was between 5 and 7.5 times higher in areas of high MTBE use compared to areas of low MTBE use. Previous work has indicated that the detection frequency of MTBE was between 2 and 5 times higher in areas of high MTBE use compared to areas of low MTBE use (Moran, Clawges, and Zogorski, 2002). The reason for the greater difference in detection frequencies between areas of high and low MTBE use for ground water, as presented in this report, is probably related to other factors, such as population density. As previously mentioned, the probability of detecting MTBE is related to population density. Further analysis revealed that, for the ground-water survey, population density was higher in the high MTBE use relative to the low MTBE use areas and that this difference was significant ($p < 0.05$). Thus, the higher population density in areas of high MTBE use relative to areas of low MTBE use probably accounts for the higher detection frequency ratios reported here.

The use of MTBE in oxygenated gasoline has resulted in higher concentrations of MTBE in ground water. When a comparison was made of the distributions of concentrations of MTBE, higher concentrations were found in areas of high MTBE use compared to areas of low MTBE use. Thus, ground water underlying areas of high MTBE use has higher detection frequencies and concentrations of MTBE compared to areas of low MTBE use.

There was no dependence of the detection frequencies of MTBE on dissolved-oxygen conditions in ground water when no assessment level was applied but there was a dependence of MTBE detection frequencies on dissolved-oxygen conditions when concentrations of MTBE greater than 0.5 $\mu\text{g/L}$ were considered. The lack of a dependence of low concentrations of MTBE on dissolved-oxygen conditions in ground water seems to support that: (1) biodegradation of low MTBE concentrations occurs in both oxic and anoxic ground-water conditions; (2) little biodegradation of low MTBE concentrations occurs in either condition, or (3) biodegradation of low MTBE concentrations occurs in oxic and/or anoxic ground-water conditions but the transformations have no effect on dissolved-oxygen concentrations. When an assessment level of

0.5 $\mu\text{g/L}$ was applied to MTBE concentrations, detection frequencies of MTBE were dependent on dissolved-oxygen conditions in ground water with a higher detection frequency in anoxic ground water compared to oxic ground water. Also, dissolved oxygen was found to be significantly associated with the probability of occurrence of MTBE at or greater than concentrations of 0.5 $\mu\text{g/L}$ when controlling for population density, use of MTBE in gasoline, and recharge in a logistic regression analysis. These results suggest that MTBE biodegradation may be occurring in oxic ground-water conditions for higher MTBE concentrations. Biodegradation of MTBE has been shown to occur under oxic conditions in both laboratory and field studies (Borden and others, 1997; Steffan and others, 1997; Bradley and others, 1999).

After standardizing the slope coefficients, the results of the logistic regression analyses indicated that three variables were most important in affecting the probability of occurrence of MTBE in ground water: population density, use of MTBE in gasoline, and recharge. As population density in the vicinity of the well increased, the probability of detecting MTBE in ground water increased. Likewise, the probability of detecting MTBE in ground water was higher in areas with high use of MTBE in gasoline compared to areas of low use. Areas of higher population density and higher use of MTBE in gasoline would be expected to be associated with larger numbers of potential point and non-point sources of MTBE to ground water. Also, as recharge increased the probability of detecting MTBE also increased. Higher recharge is likely associated with greater transport of contaminants from the surface to ground water. Anthropogenic activities in urban areas can lead to recharge rates that are higher than natural levels. This, along with increased sources, could lead to increased MTBE contamination of ground water in urban areas.

The results of the logistic regression analyses also indicated that three other variables affect the probability of occurrence of MTBE in ground water, but these have less significance in influencing MTBE occurrence. These three variables were aquifer consolidation, soil permeability, and the density of leaking underground gasoline storage tanks. The probability of detecting MTBE in ground water was higher in consolidated aquifers compared to unconsolidated aquifers. The average linear velocities of ground water through fractured consolidated aquifer materials can be quite high and higher than through unconsolidated aquifer

materials (Freeze and Cherry, 1979). Thus, contaminants that enter consolidated aquifers with fracture porosity, such as karst limestone or fractured crystalline rock, can move quickly through the aquifer system and less time is available for attenuation by biodegradation, dispersion, and diffusion.

The probability of detecting MTBE in ground water increased as soil permeability increased. Increased soil permeability likely increases the rate of transfer of contaminants from the surface to ground water. The probability of detecting MTBE in ground water increased with increasing number of leaking underground gasoline storage tanks in the vicinity of the well. Although leaking underground storage tanks might seem to be an important source for MTBE, the standardized coefficient for this variable was the lowest of all variables analyzed. This result suggests that, although they may be responsible for some occurrence of MTBE, leaking underground gasoline storage tanks may not be the primary source for most MTBE in ground water. Another important finding is that the probability of detecting MTBE was not significantly related to the density of aboveground or underground storage tanks in the vicinity of the well. This suggests that the storage of gasoline alone is not responsible for MTBE occurrence in ground water.

SUMMARY

The occurrence and concentrations of methyl *tert*-butyl ether (MTBE) and gasoline hydrocarbons were examined in three surveys—one national-scale survey for ground water, one national-scale survey for source water, and one regional-scale survey for drinking water. The overall detection frequency of MTBE for all three surveys combined was less than 10 percent using no assessment level. The overall detection frequency of MTBE in these three surveys was similar to the detection frequencies of some other volatile organic compounds (VOCs) that have much longer production and use histories. The quick arrival of MTBE in ground water relative to its production history indicates that MTBE is an important concern with respect to ground-water management.

The detection frequency of MTBE was higher in drinking water and lower in source water and ground water. The detection frequency of MTBE was higher in drinking water because public-supply wells generally have large areas contributing recharge to the well; the

location of these wells is in the Northeast, which is an area of high use of MTBE in gasoline; and drinking-water results were summarized by system. When the data for source water and ground water were limited to the same geographic extent as drinking-water data, the detection frequencies of MTBE in source water and ground water were comparable to the detection frequency of MTBE in drinking water. This indicates that the occurrence of MTBE in ground water, source water, and drinking water in the Northeast is similar when controlling for use of MTBE in gasoline.

The detection frequency of MTBE was higher in urban land-use studies compared to other study types and was higher in monitoring wells compared to other well types. The detection frequency of MTBE in monitoring wells was higher because many of these wells were sampled in urban land-use studies. The higher detection frequency of MTBE in urban land-use areas is probably related to the higher use of gasoline, and the more intense use of MTBE. Shallow ground water in urban areas appears to be at greater risk of contamination compared to deeper ground water in rural areas. However, it is not known if contamination of shallow ground water in urban areas will reach deeper aquifers used for drinking-water supply.

The median concentration of MTBE in all three surveys was relatively low. No concentration of MTBE in source water exceeded the lower limit of the U.S. Environmental Protection Agency's Drinking Water Advisory of 20 µg/L. Only one concentration of MTBE in ground water exceeded this level, and only 0.9 percent of drinking-water samples exceeded this level. Thus, most of the ground-water and drinking-water samples analyzed did not contain MTBE in concentrations that would cause organoleptic effects.

In all three surveys, the detection frequency of one or more gasoline hydrocarbon was less than the detection frequency of MTBE. The lower detection frequencies of gasoline hydrocarbons compared to MTBE are believed to be the result of differences in transport and fate properties with MTBE being more likely to be detected in ground water if released to the environment. The limitation of benzene content in reformulated gasoline appears to have resulted in lower detection frequencies of benzene in ground water in areas of high MTBE use relative to areas of low MTBE use. Because benzene is a known human carcinogen, reduction of benzene in ground water is a significant improvement in water quality.

There was a significant difference in the detection frequency of MTBE between areas of high and

low MTBE use in data from all three surveys. The detection frequency of MTBE was between 5 and 7.5 times higher in areas of high MTBE use compared to areas of low MTBE use. It is clear that the use of MTBE in oxygenated gasoline has resulted in higher detection frequencies of MTBE in ground water, source water, and drinking water. As of 2000, more than 100 million people in the United States lived in areas where MTBE was used as a gasoline oxygenate, and 92 percent of these people also lived in urban areas. Since about one-half of the people in the United States rely on ground water for drinking water (U.S. Environmental Protection Agency, 1999), as many as 45 million people may be at an increased risk of exposure to MTBE from ground-water contamination.

Using a logistic regression analysis, three variables were found to be most important in affecting the probability of occurrence of MTBE in ground water—population density, use of MTBE in gasoline, and recharge. As population density in the vicinity of the well increased, the probability of detecting MTBE in ground water increased. Likewise, the probability of detecting MTBE in ground water was higher in areas of high MTBE use in gasoline compared to areas of low MTBE use in gasoline. As recharge increased, the probability of detecting MTBE in ground water also increased.

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