United States Geological Survey
National Water Quality Assessment Program

Occurrence of the Gasoline Additive MTBE in Shallow Ground Water in Urban and Agricultural Areas

Methyl tert-butyl ether (MTBE) is a volatile organic compound (VOC) derived from natural gas that is added to gasoline either seasonally or year round in many parts of the United States to increase the octane level and to reduce carbon monoxide and ozone levels in the air. In 1993, production of MTBE ranked second among all organic chemicals manufactured in the United States. Currently, the U.S. Environmental Protection Agency (EPA) tentatively classifies MTBE as a possible human carcinogen. Health complaints related to MTBE in the air were first reported in Fairbanks, Alaska in November 1992 when about 200 residents reported problems such as headaches, dizziness, eye irritation, burning of the nose and throat, disorientation, and nausea. Similar health complaints have been registered in Anchorage, Alaska; Missoula, Montana; Milwaukee, Wisconsin; and New Jersey.

As part of the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program, concentrations of 60 VOCs were measured in samples from 211 shallow wells in 8 urban areas and 524 shallow wells in 20 agricultural areas. Chloroform and MTBE were the two most frequently detected VOCs. MTBE was detected in 27 percent of the urban wells and 1.3 percent of the agricultural wells. Concentrations ranged from less than the detection level of 0.2 µg/L (micrograms per liter) to as high as 23,000 µg/L. When detected, the median concentration of MTBE was 0.6 µg/L. MTBE was most frequently detected in shallow ground water in Denver, Colorado and urban areas in New England. In Denver, 79 percent of the samples from shallow urban wells had detectable concentrations of MTBE and in New England, 37 percent of the samples from urban wells had detectable concentrations. Only 3 percent of the wells sampled in urban areas had concentrations of MTBE that exceeded 20 µg/L, which is the estimated lower limit of the EPA draft drinking water health advisory level. Contaminant concentrations below the health advisory are not expected to cause any adverse effects over a lifetime of exposure. MTBE is on the EPA's Drinking Water Priority List, which means it is a possible candidate for future regulation.

What is MTBE and why is it used?

The Clean Air Act Amendments of 1990 mandate that compounds that add oxygen (oxygenates) be added either seasonally or year round to gasoline in specific parts of the country where concentrations of ozone in the summer or carbon monoxide in the winter exceed established air-quality standards. Oxygenates are added to increase the octane of gasoline and to improve air quality in urban areas. Oxygenates are added to more than 30 percent of the gasoline in the United States, and by the end of this decade, the Oxygenated Fuels Association has estimated that oxygenates will be added to 70 percent of the gasoline. MTBE is a commonly used oxygenate because of its low cost, ease of production, and favorable transfer and blending characteristics. It is made from methanol, which is derived primarily from natural gas. Gasoline can contain up to 15 percent MTBE by volume. In 1993, 24 billion pounds of MTBE worth about $3 billion was produced in the United States. Domestic production of MTBE and its use in the United States decreases the need for foreign oil.

Why is MTBE of interest?

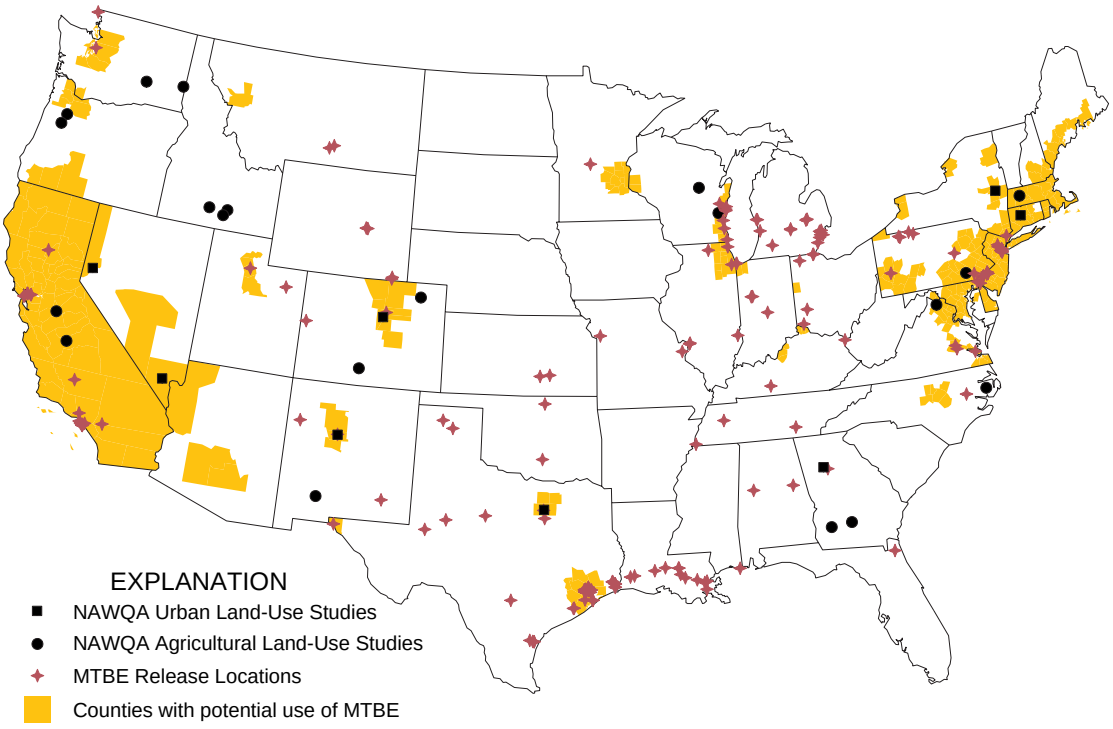
About 109 million Americans live in counties where MTBE is believed to be used (fig.1). Health complaints related to MTBE in the air were first reported in Fairbanks, Alaska in November 1992 when about 200 residents reported headaches, dizziness, irritated eyes, burning of the nose and throat, coughing, disorientation, and nausea after MTBE had been added to gasoline. Health complaints also have been registered in Anchorage, Alaska; Missoula, Montana; Milwaukee, Wisconsin; and New Jersey. Studies done by the Centers for Disease Control and Prevention in Fairbanks, Alaska; Albany, New York; and Stamford, Connecticut have shown that the concentration of MTBE in the blood is related to the concentration of MTBE in the air. People with the greatest exposure, such as gasoline service station attendants and automobile mechanics, had the largest concentrations of MTBE in their blood (ranging from less than 0.05 to 37 µg/L); however, even commuters had measurable concentrations of MTBE in their blood (ranging from less than 0.05 µg/L to 2.6 µg/L). Furthermore, the study in Fairbanks showed that among commuters there was a significant increase in the concentration of MTBE in their blood as a result of exposure to MTBE while driving. Detectable concentrations of MTBE were found in the blood of all those tested 2 months after the use of MTBE was suspended in Alaska.

What are the sources of MTBE?

All sources of MTBE released to the environment are not well documented. The release of MTBE in 1992 from industry in the United States accounted for only 0.03 percent of the MTBE that was produced. According to EPA's Toxic Release Inventory for 1992, about 94 percent of the MTBE released from industry was released to the air, 3.5 percent was discharged to surface water, and 2.5 percent was injected into wells. Releases of MTBE in addition to those from industry have not been quantified. For example, the amount of MTBE released during refueling at service stations and from mobile sources such as vehicles is unknown, but may be an important source of MTBE in the environment. Leaking underground storage tanks and spills at the land surface are also sources of MTBE in the environment.

What are the chemical properties of MTBE and its fate in the environment?

MTBE is an ether. It is a volatile, flammable, colorless liquid at room temperature, and it smells like turpentine.



MTBE release locations from U.S. Environmental Protection Agency Toxic Release Inventory for 1992.
MTBE use areas from reformulated/oxygenated fuel program areas, U.S. Environmental Protection Agency.

Figure 1. Location of urban and agricultural areas studied, and locations where MTBE may be released and used.

MTBE mixes with gasoline and is soluble in water, alcohol, and other ethers. Because of its chemical characteristics, MTBE would be expected to be found primarily in the atmosphere and in water. Results of a computer model used by Environment Canada for southern Ontario showed that 56 percent of MTBE in the environment should be found in the air, 43 percent in surface water and only about 0.5 percent in soil or streambed sediment. This model predicts where MTBE may be found in the environment but needs to be verified by environmental sampling. Although MTBE will volatilize from soils, it is also highly mobile in soil and can move into ground water. Once in ground water, MTBE resists decay when compared to other gasoline components like benzene. In surface water, MTBE is not expected to bioaccumulate in aquatic organisms.

It is hypothesized that MTBE moves with water in the hydrologic cycle (fig. 2), but more data are needed to determine the extent of the movement. MTBE is released to the air from sources such as industry and vehicles. Once in the air, MTBE can mix with precipitation that may eventually carry MTBE to the ground water or to streams. The MTBE detected in snow samples collected in Denver, Colorado by U.S. Geological Survey scientists supports this hypothesis. Alternatively, gasoline spills may directly contribute to MTBE contamination of ground water and surface water.

Where, how frequently, and at what concentrations is MTBE found in shallow ground water?

The concentrations of MTBE and 59 other VOCs were measured in samples of shallow ground water from 211 urban wells and 524 agricultural wells in 1993-94. These monitoring wells are located in 8 urban and 20 agricultural areas. These urban areas were located where MTBE was released to the environment by industry or is potentially used in gasoline. Some of the wells were constructed for the NAWQA studies, whereas others were existing wells. Wells for these studies were randomly located within specific land-use areas to allow comparison of shallow ground-water quality with land use. Urban wells were located in industrial, commercial, residential, and recreational areas, while agricultural wells were located in various crop areas.

Water-quality data from urban and agricultural areas show that MTBE occurs predominantly in shallow ground water underlying urban areas. MTBE was detected in 27 percent of urban wells, and in 1.3 percent of agricultural wells distributed across the United States, with concentrations ranging from less than the detection level of 0.2 µg/L to 23,000 µg/L. The concentrations of MTBE in ground water from eight urban areas are shown in figure 3. When detected, the median concentration of MTBE was 0.6 µg/L.

MTBE was detected in shallow ground water in all eight urban land-use studies but was detected in ground water from only 3 of 20 agricultural areas studied. For the urban areas, MTBE was most frequently detected in Denver, Colorado, and in urban areas in New England (fig. 4). In Denver, 79 percent of the shallow urban wells (23 of 29 wells) had detectable concentrations of MTBE, and in New England (specifically urban areas within Connecticut, Massachusetts, and Vermont), 37 percent of the wells (13 of 35 wells) had detectable concentrations of MTBE. Other urban areas where MTBE was detected included Reno, Nevada; Albany, New York; Dallas/Fort Worth, Texas; Las Vegas, Nevada; Atlanta, Georgia; and Albuquerque, New Mexico. Within agricultural land-use areas, MTBE was detected in southern Colorado, New England, and eastern Pennsylvania.

MTBE was the second most commonly detected VOC in water from urban wells. Of the 211 urban wells tested, 28 percent had chloroform; 27 percent had MTBE; 18 percent had tetrachloroethene; 10 percent had trichloroethene; 7 percent had cis-1,2 dichloroethene; 5 percent had 1,1-dichloroethane; and 5 percent had benzene. There are many potential sources for these other chemicals; however, 1,1-dichloroethane and benzene are used in gasoline, and chloroform has been identified in automobile exhaust.

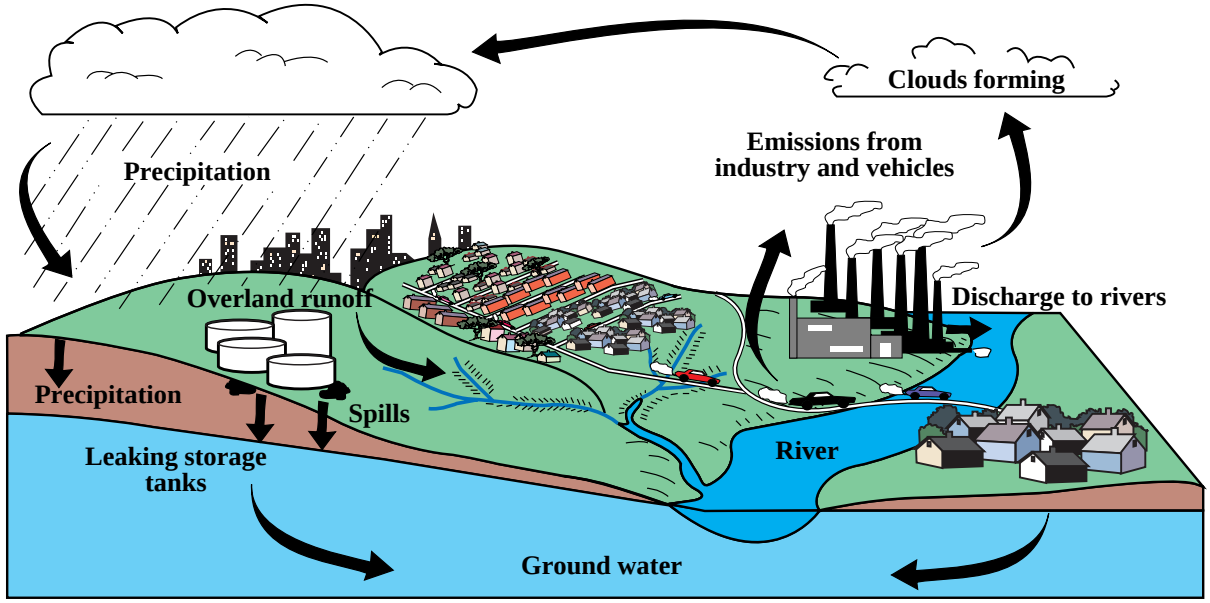


Figure 2. The movement of MTBE in the environment.

Do the concentrations of MTBE in ground water pose a threat to human health?

The EPA draft drinking water lifetime health advisory for MTBE is estimated to fall within the range of 20-200 µg/L. The health advisory is the maximum concentration in drinking water that is not expected to cause any adverse effects over a lifetime of exposure, with a margin of safety. EPA expects to issue the final health advisory in the fall of 1995. EPA tentatively classifies MTBE as a possible human carcinogen. MTBE is also on the EPA's Drinking Water Priority List which means it is a possible candidate for future regulation. There are no current Federal regulations that require municipalities to test for MTBE in drinking water.

The water sampled by U.S. Geological Survey scientists was located near the top of the water table and is the ground water most likely to show contamination from sources at the land surface. In seven of the eight urban areas studied, the sampled ground water is the uppermost part of an aquifer used for drinking water or is possibly connected to an underlying aquifer, which is used as a municipal water supply.

None of the urban wells sampled were being used as a source of drinking water. In general, public water supplies draw water from deeper parts of the ground water system

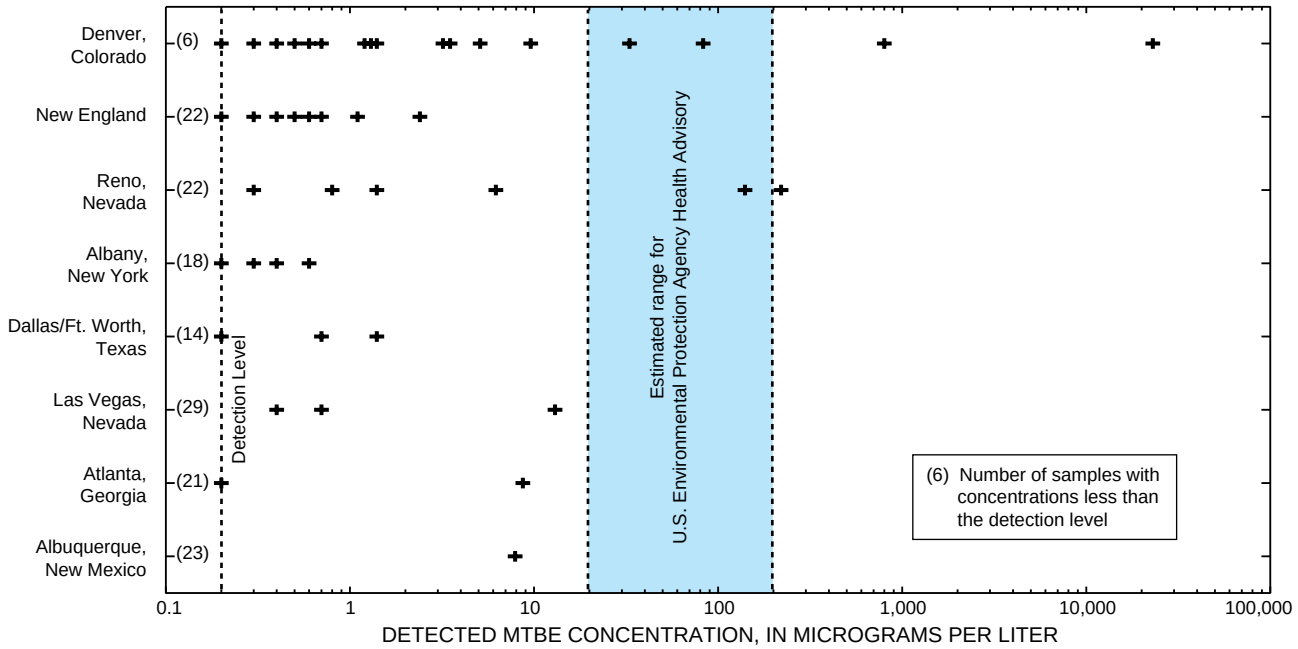


Figure 3. The concentrations of MTBE in each of the eight urban study areas.

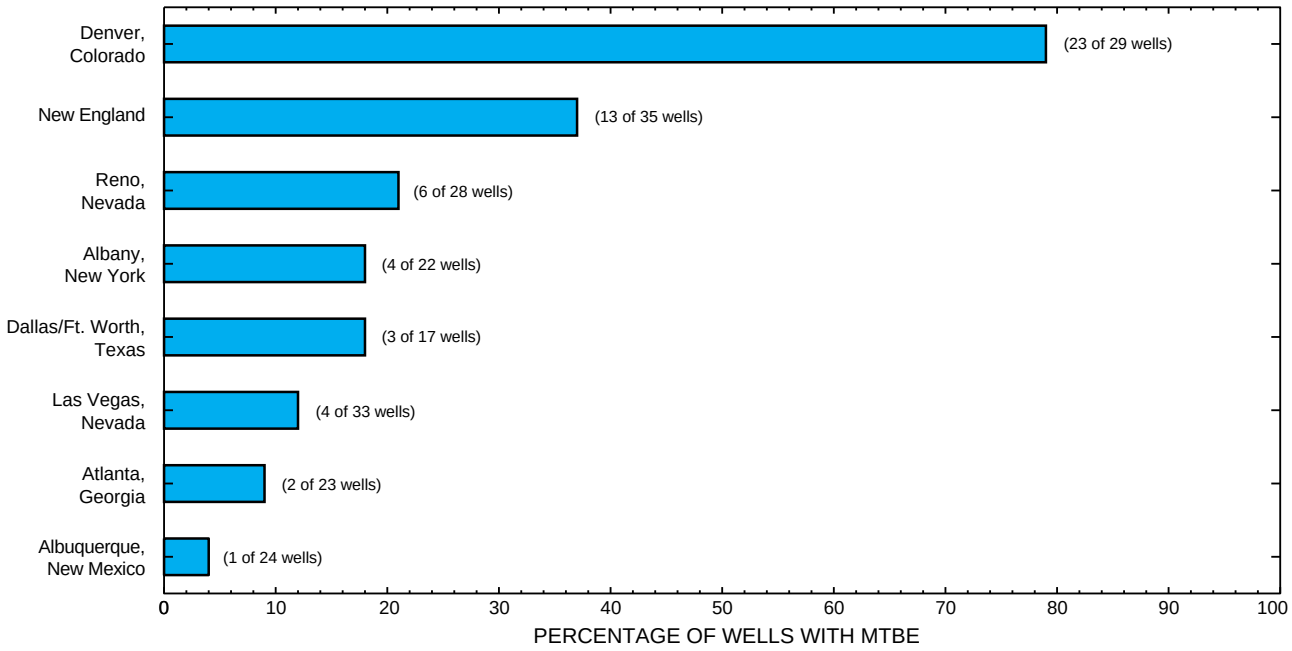


Figure 4. The frequency of detection of MTBE for each urban study area.

and there are few data showing concentrations of MTBE at these deeper depths. Of the urban monitoring wells tested, about 24 percent had concentrations of MTBE ranging from 0.2 to 20.0 µg/L, and 3 percent had concentrations exceeding 20.0 µg/L.

What are the implications of this study?

NAWQA data show that MTBE is found predominantly in shallow ground water in urban areas; however, many questions need to be answered. For example:

(1) Can MTBE in shallow ground water be traced to nonpoint mobile sources, such as vehicle emissions? Alternatively, how much MTBE in shallow ground water is due to point-source spills or leaking underground storage tanks?

(2) Do other fuel oxygenates occur in shallow ground water in urban areas?

(3) What is the fate of MTBE and other possible oxygenates in shallow ground water; will these oxygenates degrade over time due to natural processes, or will they accumulate in ground water?

(4) What are the concentrations of MTBE and other oxygenates in the air, in precipitation, and in surface water in urban areas? Is MTBE transported to ground water by infiltration of precipitation?

The U. S. Geological Survey will be working on these questions in cooperation with city and state organizations, and other Federal agencies.

Suggestions for further reading

Leahy, P.P., and Thompson, T.H., 1994, U. S. Geological Survey National Water-Quality Assessment Program: U. S. Geological Survey Open-File Report 94-70, 4 p.

Mormille, M.R., Liu, Shi, and Suflita, J.M., 1994, Anaerobic biodegradation of gasoline oxygenates--extrapolation of information to multiple sites and redox conditions: Environmental Science and Technology, v. 28, no. 9, p. 1727-1732.

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Moolenaar, R.L., Hefflin, B.J., Ashley, D.L., Middaugh, J.P., and Etzel, R.A, 1994, Methyl tertiary butyl ether in human blood after exposure to oxygenated fuel in Fairbanks, Alaska: Archives of Environmental Health, v. 49, no. 5, p. 402-409.

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Information on technical reports and hydrologic data related to NAWQA can be obtained from:
NAWQA VOC National Synthesis
U.S. Geological Survey, WRD
1608 Mt. View Rd.
Rapid City, SD 57702

Additional information on NAWQA and other U.S. Geological Survey programs can be found by accessing the NAWQA "home page" on the World Wide Web at "*http://wwwrvares.er.usgs.gov/nawqa/nawqa_home.html*."

Additional information on health effects of MTBE and drinking water regulations can be obtained by calling EPA's Safe Drinking Water Hotline 1-800-426-4791.