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Occurrence of the Gasoline Oxygenate MTBE and BTEX Compounds in Urban Stormwater in the United States, 1991-95

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Abstract

Methyl *tert*-butyl ether (MTBE) is a gasoline oxygenate. Oxygenates such as MTBE, when added to gasoline, increase the gasoline's oxygen level and decrease vehicular carbon monoxide emissions and ozone levels in the atmosphere. MTBE disperses rapidly in water, was the second most frequently detected volatile organic compound (VOC) in a study of shallow urban ground water, and is less biodegradable than common gasoline compounds, such as benzene, toluene, ethylbenzene, and total xylene (BTEX). Urban stormwater is a possible source of MTBE found in shallow ground water.

The U.S. Geological Survey (USGS) sampled stormwater in 16 cities and metropolitan areas that are required to obtain permits to discharge stormwater from their municipal storm-sewer system into surface water. Concentrations of 62 VOCs, including MTBE and BTEX compounds, were measured in 592 stormwater samples collected in these cities and metropolitan areas from 1991 through 1995. Concentration data for MTBE and BTEX compounds in stormwater were compiled and analyzed, and the findings are summarized in this report. This effort was part of an inter-agency assessment of the scientific basis and effectiveness of the Nation's oxygenated fuel program and was coordinated by the Office of Science and Technology Policy, Executive Office of the President.

MTBE was the seventh most frequently detected VOC in urban stormwater, following toluene, total xylene, chloroform, total trimethylbenzene, tetrachloroethene, and naphthalene. MTBE was detected in 6.9 percent (41 of 592) of stormwater samples collected. When detected, concentrations of MTBE ranged from 0.2 to 8.7 micrograms per liter ($\mu\text{g/L}$), with a median of 1.5 $\mu\text{g/L}$. All detections of MTBE were less than the lower limit of the U.S. Environmental Protection Agency (EPA) draft lifetime health advisory (20 $\mu\text{g/L}$) for drinking water. Eighty-three percent of all detections of MTBE in stormwater were in samples collected during the October through March season of each year (1991-95), which corresponds with the expected seasonal use of oxygenated gasoline in areas where carbon monoxide exceeds established air-quality standards. The median concentration of MTBE and benzene for all samples was statistically different and higher in samples collected during the October through March season than samples collected during the April through September season. Sixty-six percent of all MTBE detections occurred with BTEX com-

pounds, and a proportionate increase in concentrations was found when these compounds occurred together. The proportionate increase could indicate a common source of MTBE and BTEX for those samples. Toluene and total xylene were the most frequently detected BTEX compounds and the most frequently detected VOCs in these investigations. Detected concentrations of toluene and total xylene ranged from 0.2 to 6.6 $\mu\text{g/L}$ and 0.2 to 15 $\mu\text{g/L}$ with median concentrations of 0.3 and 0.4 $\mu\text{g/L}$, respectively.

Introduction

The Clean Air Act amendments of 1990 mandate seasonal or year-round use of oxygenated compounds (oxygenates) in gasoline in specific parts of the United States. Oxygenates are added to gasoline to increase the oxygen level, which enhances combustion and decreases vehicular carbon monoxide emissions. Oxygenates also reduce the need for benzene and other ozone-forming, aromatic compounds in gasoline. Oxygenates are added to gasoline during the winter months (October through March) in areas where winter concentrations of carbon monoxide exceed established air-quality standards. In select areas, oxygenates also are added to gasoline to abate ozone pollution during the summer months (April through September) as well as carbon monoxide pollution during the winter months. MTBE is the most commonly used oxygenate and is synthesized from methanol and isobutylene. MTBE is a VOC that is liquid at room temperature and is soluble in water, alcohol, and gasoline.

Oxygenated gasoline and reformulated gasoline are two classes of gasoline that contain different amounts of oxygenated compounds. Oxygenated gasoline contains no less than 2.7 percent oxygen by weight, or 14.8 percent MTBE by volume. Reformulated gasoline contains no less than 2.0 percent oxygen by weight, or 11 percent MTBE by volume. Officials have voluntarily chosen to use oxygenated gasoline to improve air quality in many areas of the United States that are in compliance with air-quality standards. MTBE and other oxygenates also have been used to enhance octane levels of gasoline since the late 1970's; however, the amount of oxygenate used is less than the amount stipulated by the Clean Air Act.

Of 60 VOCs measured in 1993 and 1994 as part of the USGS's National Water-Quality Assessment Program, MTBE was the second most frequently detected VOC in ground water sampled from 210 shallow wells and springs in 8 urban areas (Squillace and others, 1996). MTBE concentrations exceeded 20 $\mu\text{g/L}$ in 3 percent of the samples. The EPA has issued a draft lifetime health advisory for

MTBE in drinking water that ranges from 20 to 200 $\mu\text{g/L}$ (U.S. Environmental Protection Agency, 1996). The EPA is continuing to assess MTBE health data. Human-health complaints related to MTBE air exposure by some individuals have been reported in Fairbanks and Anchorage, Alaska; Missoula, Montana; Milwaukee, Wisconsin; and New Jersey. Symptoms of MTBE exposure included headaches, dizziness, irritated eyes, coughing, disorientation, and nausea.

Possible nonpoint sources of MTBE in shallow ground water include infiltration of stormwater runoff and precipitation. Possible point sources include spills on land surfaces that may enter surface water and releases from aboveground and underground gasoline storage tanks. MTBE and other oxygenates released to the environment are expected to move with water in the hydrologic cycle (fig. 1), primarily because they are highly soluble in water. Precipitation can contribute MTBE to surface water by falling directly on a body of water, by overland runoff, and from stormwater discharges. MTBE is less biodegradable than common gasoline hydrocarbons such as BTEX compounds, and although volatile, MTBE is not expected to rapidly volatilize from deep, slow-moving rivers and some streams (Zogorski and others, 1996). More data are needed to assess the extent of MTBE's movement in the hydrologic cycle.

Because of human-health, engine-performance, and water-quality concerns, the Office of Science and Technology Policy, Executive Office of the President, coordinated an interagency assessment of the scientific basis and effectiveness of the Nation's winter oxygenated gasoline program. Findings from this assessment (Zogorski and others, 1996) indicate that MTBE occurs in urban air, disperses rapidly in water, and could occur in precipitation in proportion to its concentration in the atmosphere. For a given atmospheric concentration, cooler temperatures result in higher concentrations of MTBE in precipitation than do warmer temperatures.

As part of the interagency assessment, data on VOCs in stormwater that were collected by the USGS were compiled and analyzed. This report presents a summary of the 10 most frequently detected VOCs and an analysis of the occurrence of MTBE and BTEX compounds.

Where has the USGS sampled urban stormwater for MTBE?

Stormwater studies were completed by the USGS in 11 states from 1991 through 1995 in association with local cooperators. Data were interpreted as part of an effort to document the occurrence of fuel oxygenates in urban storm-

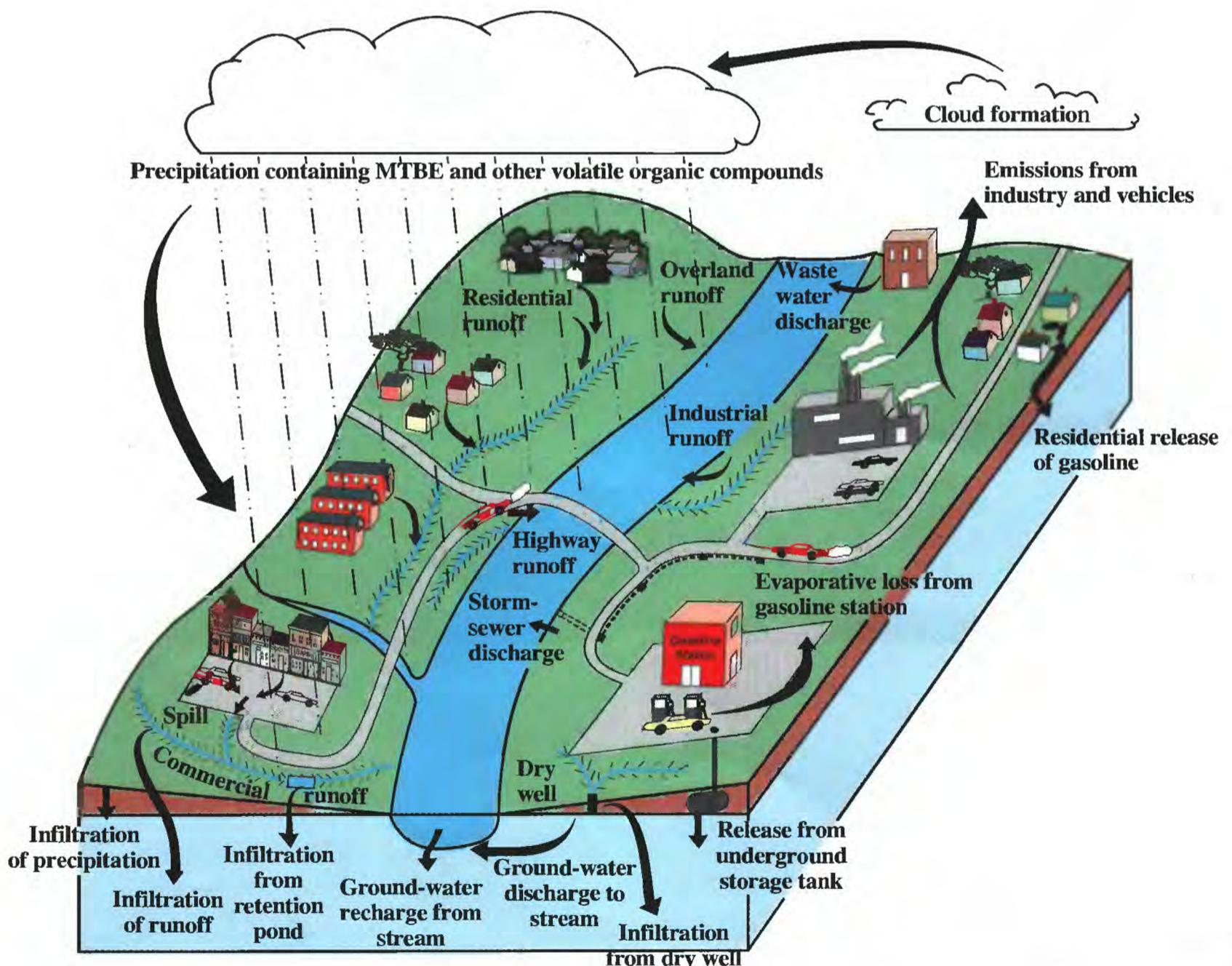


Figure 1. Movement of MTBE and other volatile organic compounds in the hydrologic cycle.

water with the most current information available. Stormwater samples collected in 16 cities and metropolitan areas with a population greater than 100,000 (fig. 2) were analyzed for BTEX compounds, MTBE (the only oxygenate analyzed), and other constituents. These cities are required by the Clean Water Act to obtain permits for stormwater discharged from municipal separate storm-sewer systems into surface water. State air-pollution officials confirmed that MTBE was used in a winter oxygenated gasoline program during the sampling period in Colorado Springs and Denver, Colorado, and Phoenix, Arizona, and was not used in an oxygenated gasoline program in the other 13 cities. In none of the cities was MTBE used in reformulated gasoline for ozone abatement. MTBE, however, may have been used in all or some of these cities to enhance the octane of gasoline.

The USGS stormwater investigations were not specifically designed to characterize gasoline oxygenates in stormwater. However, the data that were collected do provide some insights on the occurrence, or lack of occurrence, of MTBE and BTEX compounds in stormwater in the cities sampled. The design of each investigation differed depending on the requirements of each EPA Region and the extent of monitoring desired by each municipality. Samples were collected from a variety of stormwater conveyances, such as culverts, concrete pipes, lined ditches, and channels. The drainage area of sampled sites typically was small and ranged from 0.005 to 10.7 square miles. Each site had a predominant land use including residential, commercial,

industrial, or highway. Samples generally were collected by hand-dipping VOC sample bottles in stormwater, usually within the first 2 hours of storm runoff. One sample was collected during each storm event with the exception of Colorado Springs, Colorado, where two to four samples were collected (von Guerard and Weiss, 1995). For this report, each sample from Colorado Springs was included in the data analyses. All samples were analyzed at the USGS National Water-Quality Laboratory by gas chromatography/mass spectrometry (Rose and Schroeder, 1995).

Where, how frequently, and at what concentration was MTBE found in urban stormwater?

Concentrations of 62 VOCs were measured in 592 stormwater samples collected in 16 cities from 1991 through 1995. MTBE was the 7th most frequently detected VOC in urban stormwater, following toluene, total xylene, chloroform, total trimethylbenzene, tetrachloroethene, and naphthalene (table 1). MTBE was detected in one or more stormwater samples in eight cities—Atlanta, Georgia, Baton Rouge, Louisiana, Birmingham, Alabama, Colorado Springs and Denver, Colorado, Dallas/Fort Worth and San Antonio, Texas, and Phoenix, Arizona. Detectable concentrations and frequency of detection for MTBE in these eight cities are shown in figure 3.

MTBE detection frequencies were calculated for the entire study period and for the October through March and

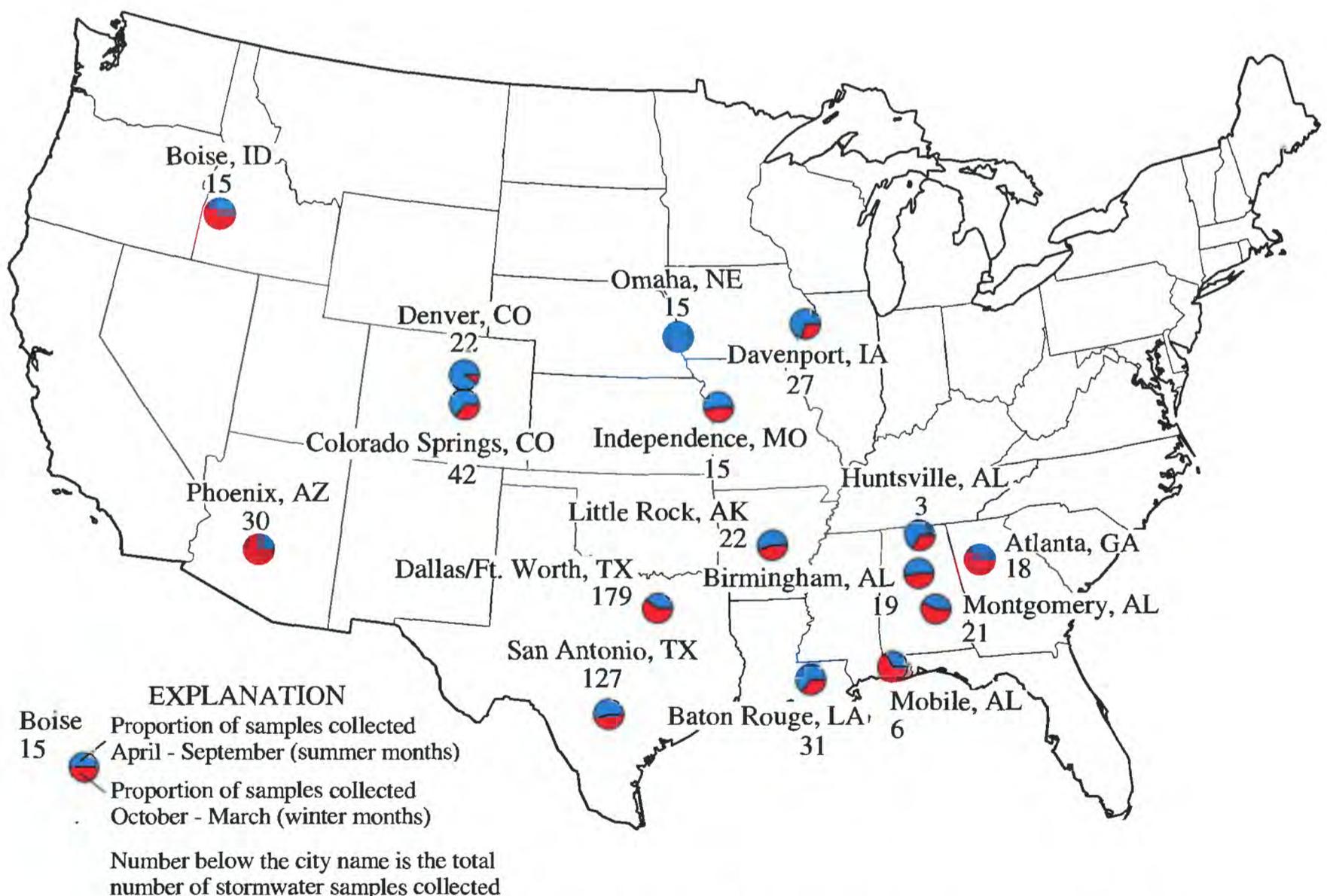


Figure 2 . Cities and metropolitan areas where MTBE was sampled in urban stormwater, 1991-95.

April through September seasons for each stormwater project. The October through March season corresponds with the expected winter use of oxygenated gasoline in areas where carbon monoxide exceeds established air-quality standards. Oxygenated gasoline is not expected to be used during the April through September season in areas where carbon monoxide exceeds air-quality standards. Three-hundred five (305) of the samples were collected during the April through September season, and 287 samples were collected during the October through March season. MTBE was detected in 41 of the 592 stormwater samples, or 6.9 percent (fig. 3). Concentrations of MTBE in stormwater for all samples, including those less than the minimum reporting level (MRL), ranged from less than the MRL to 8.7 $\mu\text{g/L}$, with a median concentration less than the MRL. A detectable concentration is one that is greater than or equal to the MRL. All detections of MTBE were less than the lower limit of the EPA draft lifetime health advisory (20 $\mu\text{g/L}$) for drinking water. For those samples in which MTBE was detected, the concentrations ranged from 0.2 to 8.7 $\mu\text{g/L}$, with a median of 1.5 $\mu\text{g/L}$. Eighty-three percent, or 34 of 41 detections, occurred during the October through March season when MTBE would likely be used in greater amounts in areas where carbon monoxide concentrations exceeded air-quality standards.

Table 1. Statistical summary of the 10 most frequently detected volatile organic compounds in urban stormwater in the United States, 1991-95

[$\mu\text{g/L}$, micrograms per liter]

VOC	Minimum detected concentration ($\mu\text{g/L}$)	Maximum detected concentration ($\mu\text{g/L}$)	Median detected concentration ($\mu\text{g/L}$)	Frequency of detection (percent)
Toluene	0.2	6.6	0.3	23.2
Total xylene	0.2	15	0.4	17.5
Chloroform	0.2	7.0	0.7	13.4
Total trimethylbenzene	0.2	15	0.3	12.4
Tetrachloroethene	0.2	42	0.6	8.0
Naphthalene	0.2	5.1	0.3	7.4
MTBE	0.2	8.7	1.5	6.9
Dichloromethane	0.2	13	0.3	5.9
Bromodichloromethane	0.2	2.8	0.6	5.8
Ethylbenzene	0.2	2.0	0.3	5.0

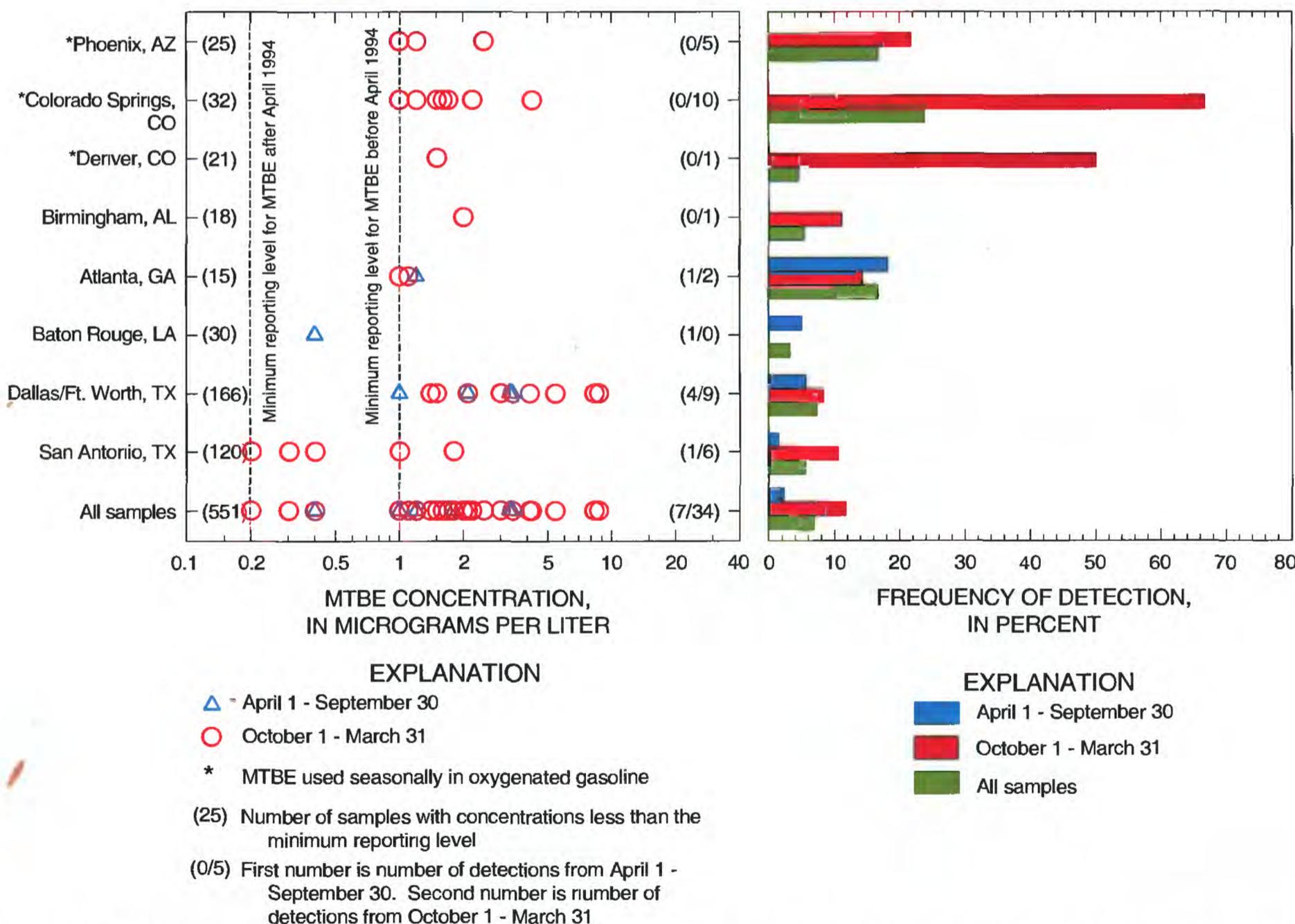


Figure 3. Concentration and frequency of detection of MTBE in urban stormwater from eight cities and metropolitan areas, 1991-95.

The MRL for the analytical technique used for MTBE was reduced from 1.0 to 0.2 µg/L in April 1994. However, most of the stormwater samples collected in the USGS investigations described here were analyzed prior to this change. The high MRL of 1.0 µg/L for MTBE for most of the samples censors data with low concentrations. A lower MRL for MTBE would likely result in increased frequency of detection and a lower median detectable concentration. The MRL was different for some stormwater samples because they had to be diluted prior to analysis, which resulted in a higher reporting level. Eighty-three percent of the 592 samples were not diluted and were analyzed with a MRL of 1.0 µg/L. Eleven percent were not diluted and were analyzed with a MRL of 0.2 µg/L. Six percent of the samples were diluted and were analyzed with a MRL that ranged from 0.4 to 100 µg/L.

The median concentration of MTBE for all samples was shown to be statistically different and higher during the October through March season in comparison to the April through September season. The probability of the median concentration of MTBE being the same during these two seasons is less than 1 in 10,000. The strong seasonal detection pattern may be attributed to the increased volume and use of MTBE in gasoline during the oxygenated gasoline season, longer atmospheric half-lives of MTBE during the winter, and (or) to the higher solubility and decreased volatility (the tendency of a liquid or solid to change into the gaseous state) of MTBE in stormwater at winter temperatures.

For each of the three cities (Phoenix, Arizona, Colorado Springs, Colorado, and Denver, Colorado) with known MTBE use, MTBE was detected only in stormwater samples collected during the season when oxygenated gasoline was in use (fig. 3). MTBE was detected in 16 of 40 (40 percent) samples and concentrations ranged from 1.0 to 4.2 µg/L, with a median concentration of 1.5 µg/L.

Detection of MTBE in cities confirmed not to use oxygenated fuel may be attributable to the use of MTBE in gasoline as an octane enhancer. These cities include Atlanta, Georgia, Baton Rouge, Louisiana, Birmingham, Alabama, and Dallas/Fort Worth and San Antonio, Texas.

How does the occurrence of MTBE relate to other gasoline components?

Because of their toxicity, the common gasoline compounds (BTEX compounds) historically have been of concern when gasoline is spilled into surface waters. MTBE, however, is approximately 40 times more water soluble than BTEX compounds at room temperature. Once MTBE enters a surface water, it is expected to volatilize at rates similar to BTEX compounds in deep, slow-moving streams or rivers (Zogorski and others, 1996). However, MTBE is expected to persist longer than BTEX compounds in shallow, fast-moving streams or rivers.

Seventy-nine percent (467) of the 592 stormwater samples were collected from the eight cities that had at least one detectable concentration of MTBE. Thirty-two percent (148) of the 467 samples had detectable concentrations of either MTBE or BTEX (fig. 4). Among the 148 stormwater samples, 18 percent contained both MTBE and BTEX compounds, 72 percent contained only BTEX compounds, and 10 percent contained only MTBE. Sixty-six percent of the

41 MTBE detections were in samples that also had detectable concentrations of BTEX compounds. A proportionate increase in concentration was found when these compounds were detected together, which could indicate a common source of MTBE and BTEX for these samples. Toluene and total xylene were the most frequently detected BTEX compounds and were also the most frequently detected VOCs in these investigations. When detected, concentrations of toluene and total xylene ranged from 0.2 to 6.6 µg/L and 0.2 to 15 µg/L with median concentrations of 0.3 and 0.4 µg/L, respectively. BTEX compounds were analyzed with a MRL of 0.2 µg/L throughout the study.

Detections of toluene, total xylene, and ethylbenzene did not follow a seasonal detection pattern. The median concentrations for these compounds were shown to be statistically similar during the October through March season in comparison to the April through September season. The detection of benzene, however, followed a seasonal detection pattern similar to that for MTBE. The probability of the median concentrations of benzene being the same during these two seasons is about 1 in 3,300. The strong seasonal detection pattern for benzene may be attributed, in part, to the higher solubility and decreased volatility of benzene during colder winter temperatures.

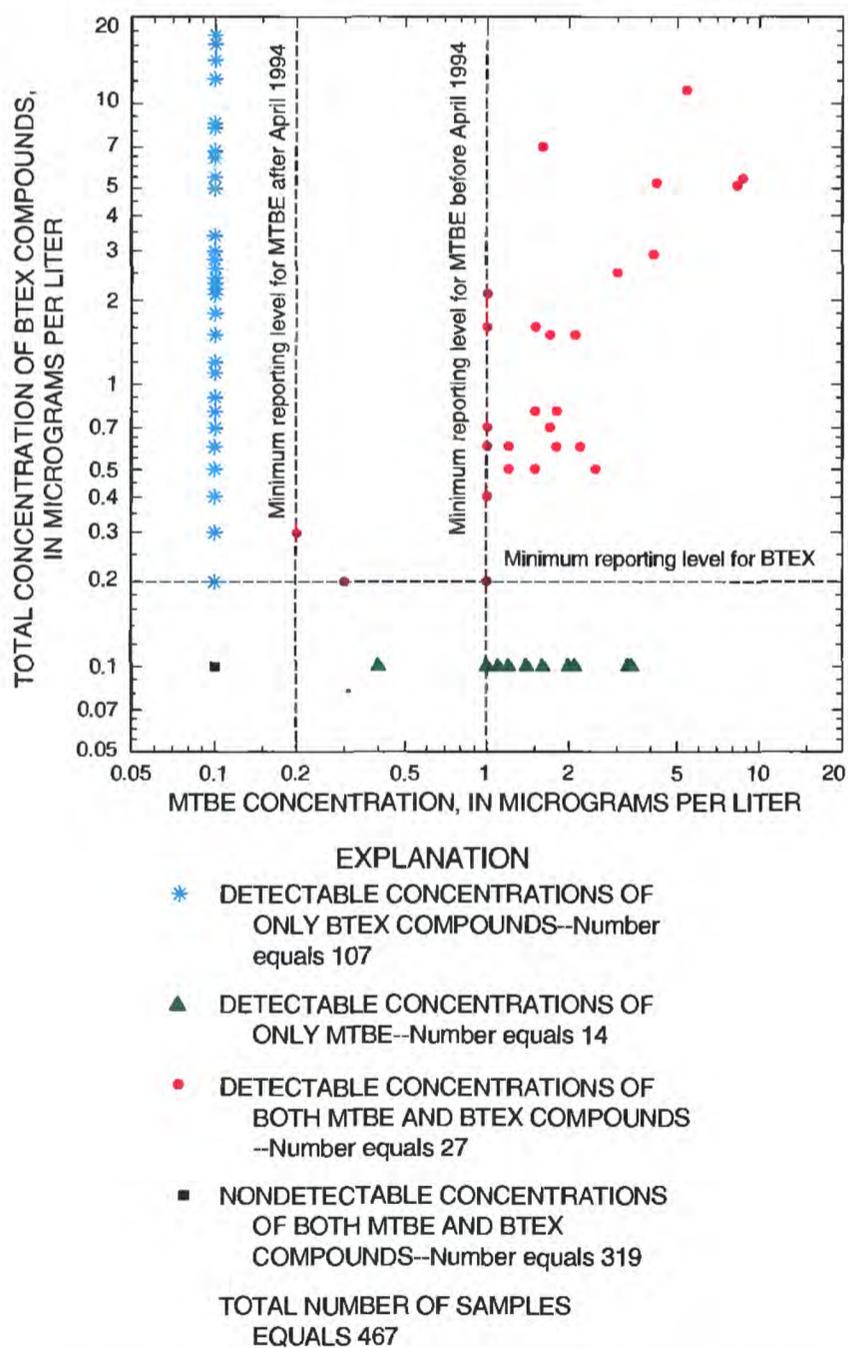


Figure 4. Total concentration of BTEX compounds versus concentration of MTBE for eight cities that had detectable concentrations of MTBE in urban stormwater, 1991-95.

Summary and Remaining Questions

When gasoline containing MTBE is mixed with water, MTBE concentrations in water will be about 40 times larger than the common gasoline compounds (BTEX compounds) at room temperature. MTBE is added to gasoline to increase the oxygen level, which enhances combustion and decreases carbon monoxide emissions. In some areas where concentrations of carbon monoxide exceed established air-quality standards, oxygenates are added to gasoline during the winter months (October through March). Oxygenates, such as MTBE, reduce the need for benzene, and other ozone-forming, aromatic compounds in gasoline. Once MTBE enters a surface water, it is expected to volatilize at rates similar to BTEX compounds in deep, slow-moving streams or rivers. However, MTBE is expected to persist longer than BTEX compounds in shallow, fast-moving streams or rivers.

MTBE was detected in 6.9 percent (41) of 592 stormwater samples collected in 16 cities and metropolitan areas from 1991 through 1995. When detected, concentrations of MTBE ranged from 0.2 to 8.7 $\mu\text{g/L}$, with a median of 1.5 $\mu\text{g/L}$. All concentrations of MTBE were less than the lower limit of the EPA draft lifetime advisory (20 $\mu\text{g/L}$) for drinking water. Toluene and total xylene were the most frequently detected BTEX compounds and, of 62 VOCs analyzed, the most frequently detected VOCs. When detected, concentrations of toluene and total xylene ranged from 0.2 to 6.6 $\mu\text{g/L}$ and 0.2 to 15 $\mu\text{g/L}$ with median concentrations of 0.3 and 0.4 $\mu\text{g/L}$, respectively. Eighty-three percent of all detected concentrations of MTBE occurred during the October through March season, which corresponds with the expected seasonal use of oxygenated gasoline in areas where carbon monoxide exceeds established air-quality standards. Forty percent of stormwater samples that were collected during the October through March season in areas with confirmed use of oxygenated gasoline contained detectable concentrations of MTBE. The median concentration of MTBE and benzene for all samples was statistically different and higher for samples collected during the October through March season than for those collected during the April through September season. Sixty-six percent of all MTBE detections occurred with BTEX compounds, and the proportionate increase in concentrations when these compounds occurred together could indicate a common source.

These data raise questions that remain to be answered because these stormwater investigations were not designed specifically to characterize the occurrence, sources, and behavior of oxygenated gasoline components in stormwater. These include:

(1) What are the ranges and seasonal distributions of concentrations of MTBE in stormwater, including municipal separate-storm-sewer systems and combined sewer overflows, in other urban areas of the United States?

(2) What is the persistence of MTBE in streams or rivers that receive stormwater runoff? Are the concentrations in the receiving stream a cause for concern about potential effects on aquatic life? Similarly, what effect, if any, does MTBE have on public water supplies from surface-water sources?

(3) What proportion of MTBE that is detected in urban stormwater is contributed by precipitation compared to that contributed by overland runoff? How much MTBE is con-

tributed to surface water by precipitation that falls directly on larger bodies of water such as reservoirs and lakes?

(4) Do other oxygenates react similarly to MTBE in the hydrologic cycle and occur in stormwater?

(5) Is land use an important factor in the occurrence of MTBE or BTEX compounds in urban stormwater?

(6) Is stormwater recharge and (or) precipitation that contains VOCs an important source of MTBE to ground water in urban environments?

The U.S. Geological Survey continues to work on these questions in cooperation with city, state, and other Federal agencies.

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Suggestions for Further Reading

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