IDENTIFYING THE USAGE PATTERNS OF METHYL TERT-BUTYL ETHER (MTBE) AND OTHER OXYGENATES IN GASOLINE USING GASOLINE SURVEYS

By

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Methyl *tert*-butyl ether (MTBE) is commonly added to gasoline in the United States for octane enhancement and as a fuel oxygenate. It is used in large quantities each year to reduce levels of ozone and carbon monoxide in areas where air quality standards have not been attained. In 1998, 11.9 billion liters of MTBE were produced in the U.S. MTBE has been detected frequently in surface and ground water in areas that use it as a fuel oxygenate, causing concern about water quality in these areas. Understanding the relations between MTBE occurrence and its usage is important for determining if regulations meant to improve the Nation's air quality have resulted in inadvertent, detrimental effects on water quality. To understand how the occurrence of MTBE in surface and ground water relates to its use, it is necessary to know the usage patterns in areas where water samples have been analyzed.

MTBE has been used in gasoline for octane enhancement since the late 1970's when the use of tetraethyl lead was phased out. The use of fuel oxygenates, or compounds that contain oxygen, was expanded as a result of the enactment of the Clean Air Act (CAA) Amendments of 1990. The CAA Amendments mandate that oxygen must be added to gasoline in areas that do not meet National Ambient Air Quality Standards (NAAQS) for carbon monoxide and ozone. The two gasoline programs of the CAA Amendments that require oxygenate use are: 1) the Oxygenated Fuels Program (OXY) in which gasoline must contain 2.7% oxygen by weight during the cold season in areas that fail to meet NAAQS for carbon monoxide, and 2) the Reformulated Gasoline Program (RFG) in which gasoline must contain 2% oxygen by weight year-round in areas having the highest levels of tropospheric ozone.

The CAA Amendments do not specify which oxygenate must be added to gasoline but the one most commonly used is MTBE. To meet the oxygen requirements of the CAA Amendments, gasoline in OXY fuels areas must contain 15% MTBE by volume, and gasoline in RFG areas must contain 11% MTBE by volume. Although MTBE is the most commonly used oxygenate, it is not used in all RFG or OXY areas. Ethanol is the second most commonly used fuel oxygenate. In 1998, 5.3 billion liters of ethanol were produced. It generally may be assumed that ethanol is used most frequently in OXY areas to achieve oxygen requirements whereas MTBE is used most frequently in RFG areas to achieve oxygen requirements. Other alkyl ether oxygenates are used to achieve the oxygen requirements of the CAA Amendments. These include *tert*-amyl methyl ether (TAME), diisopropyl ether (DIPE), and ethyl *tert*-butyl ether (ETBE), in order of decreasing use.

Knowing that an area is designated as RFG or OXY can give some insight into the type of oxygenate being used, but this information alone cannot specifically determine which oxygenate is used in specific metropolitan areas and in what amounts. Data on the volumes of oxygenates and other compounds in gasoline are available from several sources collectively referred to here as gasoline surveys. The gasoline surveys provide the most definitive knowledge of which oxygenate, if any, and what volumes of that oxygenate are being used in various areas of the country. This information is important in water-quality assessments for relating the detection of MTBE in water to patterns of usage of MTBE in gasoline.

Table 1 summarizes general information on three surveys that have been conducted by 1) the National Institute for Petroleum and Energy Research (NIPER), 2) the Motor Vehicle Manufacturers Association (MVMA), and 3) the U.S. Environmental Protection Agency (USEPA). In general, the surveys collected data on samples of various grades and blends of gasoline from selected cities throughout the country. The samples were tested for physical properties and constituents including octane number, specific gravity, and volumes of olefins, aromatics, benzene, alcohols, and various ether oxygenates. The purpose of the NIPER survey is generally to provide comparative information to interested companies on the physical and chemical properties of fuels. The purpose of the USEPA survey is to verify that oxygen content in gasoline is sufficient to meet the USEPA RFG program requirements.

Table 1. General characteristics of gasoline surveys. [MTBE, methyl *tert*-butyl ether]

Name of survey	Agency conducting survey	Geographic coverage	Time span of analysis for MTBE and other oxygenates	Number of samples	Participation
National Institute for Petroleum and Energy Research (NIPER) survey	U.S Department of Energy	An average of 66 cities throughout the U.S. each year	1990-1999	Thousands each year	Voluntary by companies interested in fuel comparisons
Motor Vehicle Manufacturers Association (MVMA) National gasoline survey	Motor Vehicle Manufacturers Association	23 cities throughout the U.S.	Summer of 1988 to winter of 1994-1995	395 in the winter of 1988-1989	Unknown
USEPA RFG survey	Reformulated Gasoline Survey Association for the U.S. Environmental Protection Agency	23 metropolitan areas throughout the U.S.	1995-1999	Thousands each year	Voluntary by members of the Reformulated Gasoline Survey Association, a group of refiners, importers, and blenders of gasoline

The data in each survey has its own utility based on the type of assessment that is undertaken. The NIPER survey contains data for the greatest number of cities and samples analyzed. In addition, the raw NIPER data are available in computer files that facilitate analyses of the relations between the occurrence of MTBE in surface or ground water and the use of MTBE in gasoline. Data on the proportion of oxygenates in gasoline were initially reported by the NIPER survey for 1990-1991, and data on the proportions of individual ether oxygenates in gasoline have been reported since the summer of 1993. Data from the MVMA survey help to fill in gaps in the NIPER data and to extend information on oxygenate use prior to 1990. Also, because many of the cities sampled for the MVMA survey overlap with cities sampled for the NIPER survey, it is possible to make comparisons of data from the two surveys and evaluate variability in the amounts of oxygenates used in a metropolitan area. The USEPA RFG survey provides data on the proportion of oxygenates used in gasoline in RFG areas.

The USEPA also collects information on the proportion of oxygenates in gasoline in OXY areas. USEPA regional offices, through contacts within individual state energy offices, compile this information from state officials who are familiar with the proportions of oxygenates used in gasoline within their states via surveys of local refiners, blenders, importers, and distributors of gasoline. This information is compiled for each metropolitan area required to use oxygenated fuels in the winter for the OXY program.

Figure 1 shows areas of the country designated by the USEPA as RFG and also shows metropolitan areas where MTBE comprised 9-13% of gasoline by volume. The volume of MTBE in gasoline was determined from the NIPER survey for 1998 by taking a median of all sample values for that year. The areas designated as RFG include both mandatory and voluntary participation in the program as well as areas that have been in the program previously but are not now. Metropolitan areas with low MTBE use (0-3%) are believed to be using MTBE primarily for octane enhancement and are not shown in this figure. Figure 2 shows areas of the country designated by the USPEA as OXY and also metropolitan areas where ethanol comprised 8-11% of gasoline by volume. The volume of ethanol in gasoline was determined from the NIPER survey for January and February of 1998 by taking a median of all sample values during those two months. Figure 2 also shows areas that have been in the OXY program previously but are not now. Metropolitan areas with low ethanol use (0-1%) are believed to be using ethanol primarily for octane enhancement and are not shown in this figure.

Metropolitan areas shown in figures 1 and 2 are delineated by the boundaries of U.S. Bureau of the Census Consolidated Metropolitan Statistical Areas and Metropolitan Statistical Areas in combination with data on population density identifying urban areas. RFG and OXY areas are displayed as counties within metropolitan areas that have been identified by USEPA as participating in these programs. In some instances only portions of a county are within a program area; however, these boundaries are not available and the full county is shown. For these reasons, metropolitan areas shown on these figures do not overlap exactly with RFG and OXY areas.

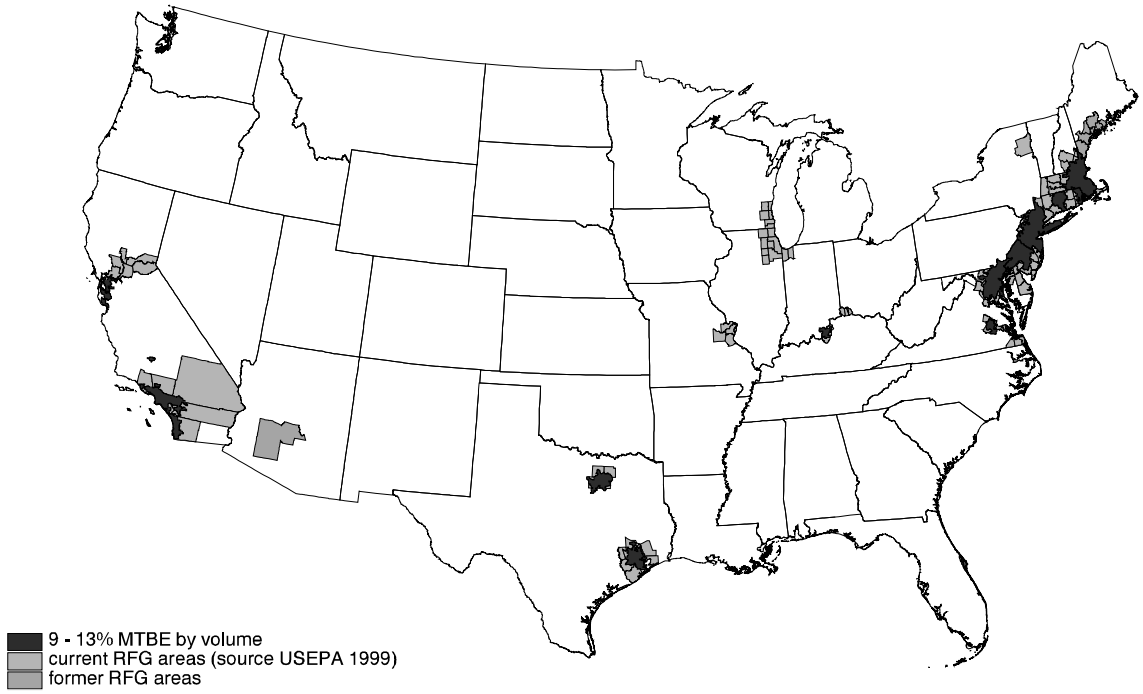

Figure 1. Areas designated as RFG and metropolitan areas where MTBE content in gasoline is 9 to 13% by volume (NIPER data, 1998 median).

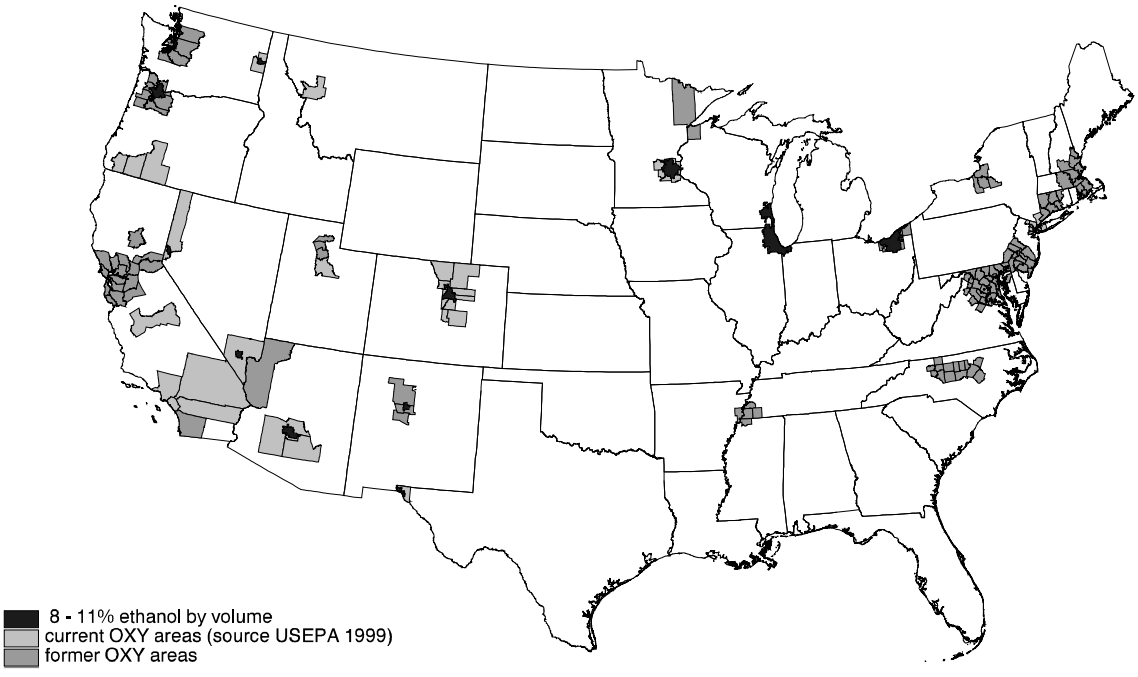

Figure 2. Areas designated as OXY and metropolitan areas where ethanol content in gasoline is 8 to 11% by volume (NIPER data, January and February 1998 median).

There is generally good agreement between the areas designated as RFG and metropolitan areas that have high MTBE use (9-13% by volume) in gasoline (fig. 1). However, some cities in RFG areas, for example Chicago, IL, use another fuel oxygenate such as ethanol (fig. 2). Other cities or areas have voluntarily entered (opted in) or removed (opted out) themselves from the RFG program or have been redesignated into or out of the program. For example, Phoenix, AZ, voluntarily entered the RFG program in 1997 and opted out in June 1998. Areas of southern Maine voluntarily entered the RFG program and opted out in 1999. There is also generally good agreement between the areas designated as OXY and the metropolitan areas that have high ethanol use (8-11% by volume). This confirms the general assumption that OXY areas primarily use ethanol to provide oxygen in gasoline.

The use of ethanol in many OXY areas is confirmed by information compiled by the USEPA. The following cities are in OXY areas and use only ethanol to achieve oxygen requirements: Minneapolis, MN, Las Vegas, NV, El Paso, TX, and Spokane, WA. Some cities in the OXY program are using a combination of ethanol and MTBE and/or TAME to meet oxygen requirements. One example is Denver, CO that, in the winter of 1998-1999, used a mixture of ethanol, TAME and MTBE to meet oxygen requirements.

An example of the utility of gasoline survey data to water-quality assessments is analyses of ground-water data from the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program. Using NAWQA data, the percent occurrence of MTBE in ground water in metropolitan areas that use substantial amounts of MTBE (> 5% by volume) was about 21%, compared to about 2% in areas that do not use substantial amounts of MTBE (≤ 5% by volume). When several other factors are considered in a logistic regression model including MTBE usage in RFG or OXY gasoline areas (≥ 3% by volume) as a factor, a 4-6 fold increase in the detection frequency of MTBE in ground water is found when compared to areas that do not use MTBE or use it only for octane enhancement (< 3% by volume).

Overall, the usage pattern of fuel oxygenates, and especially of MTBE, across the country is complex and changes with time. Although the gasoline survey data are useful in distinguishing amounts of MTBE in gasoline between various urban areas, they are applicable only to metropolitan areas at the present time. In water-quality assessments, areas outside of metropolitan areas are simply assigned as having low or unknown MTBE use. However, locations that are close to, but not within, an urban area that is designated as RFG or OXY may be using gasoline containing a high percentage of MTBE if they receive the same gasoline blend as the nearby city. In addition, the extent of the metropolitan boundaries used for the gasoline surveys is not clear in many cases. If the boundaries of cities, as defined by gasoline surveys, were more clearly delineated and if a random sampling of smaller cities also were included, the data in these surveys would have much greater value to water-quality assessments.