

Design of a National Survey of Methyl *tert*-Butyl Ether and Other Volatile Organic Compounds in Drinking-Water Sources

By Tamara Ivahnenko, Stephen J. Grady, and Gregory C. Delzer

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FOREWORD

The U.S. Geological Survey (USGS) is committed to serve the Nation with accurate and timely scientific information that helps enhance and protect the overall quality of life, and facilitates effective management of water, biological, energy, and mineral resources. Information on the quality of the Nation's water resources is of critical interest to the USGS because it is so integrally linked to the long-term availability of water that is clean and safe for drinking and recreation and that is suitable for industry, irrigation, and habitat for fish and wildlife. Escalating population growth and increasing demands for the multiple water uses make water availability, now measured in terms of quantity *and* quality, even more critical to the long-term sustainability of our communities and ecosystems.

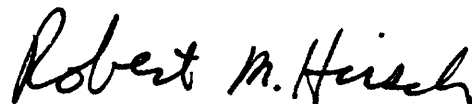
The USGS implemented the National Water-Quality Assessment (NAWQA) Program to support national, regional, and local information needs and decisions related to water-quality management and policy. Shaped by and coordinated with ongoing efforts of other Federal, State, and local agencies, the NAWQA Program 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. NAWQA results can contribute to informed decisions that result in practical and effective water-resource management and strategies that protect and restore water quality.

Since 1991, the NAWQA Program has implemented interdisciplinary assessments in more than 50 of the Nation's most important river basins and aquifers, referred to as Study Units. Collectively, these Study Units account for more than 60 percent of the overall water use and population served by public water supply, and are representative of the Nation's major hydrologic landscapes, priority ecological resources, and agricultural, urban, and natural sources of contamination.

Each assessment is guided by a nationally consistent study design and methods of sampling and analysis. The assessments thereby build local knowledge about water-quality issues and trends in a particular stream or aquifer while providing an understanding of how and why water quality varies regionally and nationally. The consistent, multi-scale approach helps to determine if certain types of water-quality issues are isolated or pervasive, and allows direct comparisons of how human activities and natural processes affect water quality and ecological health in the Nation's diverse geographic and environmental settings. Comprehensive assessments on pesticides, nutrients, volatile organic compounds, trace metals, and aquatic ecology are developed at the national scale through comparative analysis of the Study-Unit findings.

The USGS places high value on the communication and dissemination of credible, timely, and relevant science so that the most recent and available knowledge about water resources can be applied in management and policy decisions. We hope this NAWQA publication will provide you the needed insights and information to meet your needs, and thereby foster increased awareness and involvement in the protection and restoration of our Nation's waters.

The NAWQA Program 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 Program, therefore, depends extensively on the advice, cooperation, and information from other Federal, State, interstate, Tribal, and local agencies, non-government organizations, industry, academia, and other stakeholder groups. The assistance and suggestions of all are greatly appreciated.



Robert M. Hirsch
Associate Director for Water

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CONVERSION FACTORS

	Multiply	By	To obtain
acre-foot		1,233	cubic meter
cubic foot per second		0.02832	cubic meter per second
foot		0.3048	meter
gallon		3.785	liter
inch		2.54	centimeter
mile		1.609	kilometer
million gallons per day		0.04381	cubic meter per second
square foot		0.09290	square meter

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ABSTRACT

The U.S. Geological Survey (USGS), in collaboration with the Metropolitan Water District of Southern California (MWDSC) and the Oregon Graduate Institute of Science and Technology (OGI) in Beaverton, Oregon, is designing a survey of the frequency of detection, concentration, and distribution of methyl *tert*-butyl ether (MTBE), other ether gasoline oxygenates, their degradation products, and other volatile organic compounds (VOCs) in source water used by community water systems (CWSs) in the United States. This national survey is sponsored by the American Water Works Association Research Foundation.

The survey will be accomplished in two stages. The first stage, termed the Random Source-Water Survey, will determine the frequency of detection and the range in concentrations of MTBE, three other ether gasoline oxygenates, and 62 other VOCs in drinking-water sources through a statistically stratified design for sampling CWSs by the total number of systems within five population served-size categories, source of water (ground or surface water), and the total number of people served by each of the source-size categories presently used within the United States. A total of 1,000 CWSs that will represent the more than 54,000 CWSs from all 50

States, Native American Lands, and Puerto Rico will be sampled. The 1,000 source-water samples will be distributed to allocate 613 samples to ground-water-supplied CWSs (wells, springs, and galleries) and the remaining 387 samples to surface-water-supplied CWSs (rivers, aqueducts, canals, lakes, and reservoirs). Environmental samples and field blanks will be collected by CWS personnel. Samples will be analyzed by the MWDSC using U.S. Environmental Protection Agency approved method 524.2. Ancillary information about the participating CWSs and their sources will be collected to allow additional statistical analysis of the water-quality data.

The second stage, termed the Focused Source-Water Survey, will be based on factors that appear or are known to be related to frequent detection of MTBE and other VOCs in source water. CWSs located in hydrologic, climatic, and/or demographic settings that are suspected or known to be vulnerable to MTBE contamination will be selected for sampling. Large CWSs that have source water suspected of having concentrations of MTBE, are located in 14 metropolitan areas with populations greater than 250,000, and use reformulated gasoline (RFG) will be selected initially. States not located in RFG areas may also have areas with a high detection frequency of MTBE in ground water at regulated gasoline

release sites. Discussions with drinking-water officials, water suppliers, and USGS personnel will provide a better understanding of the risk of MTBE releases to source water in these States. Additional suspected source waters will be identified through these discussions.

Data on samples of source water with known concentrations of MTBE will be obtained from recently completed or ongoing sampling activities, including the Random Source-Water Survey, and from water-quality monitoring in individual States. Approximately 480 samples will be collected from 80 wells, 40 reservoirs, and 20 rivers across the United States. All samples in the Focused Source-Water Survey will be collected by USGS personnel using USGS sampling protocols. Samples for the Focused Source-Water Survey will be analyzed by the MWDSC for MTBE, three other ether gasoline oxygenates, and 62 other VOCs. Duplicate samples will be collected with about one-half of the Focused Source-Water samples and analyzed for oxygenate degradation products by OGI. As with the Random Source-Water Survey, ancillary information for the Focused Source-Water Survey will be collected to allow additional statistical analysis of MTBE and other VOC data.

INTRODUCTION

Methyl *tert*-butyl ether (MTBE) is the most commonly used gasoline oxygenate in the United States, where it is used not only to improve air quality in large metropolitan areas but also as an octane enhancer. MTBE has been used nationwide since 1979 at low concentrations (about 1 to 2 percent by volume) to enhance octane in conventional gasoline. The 1990 Clean Air Act Amendments mandated the use of special blends of gasoline containing oxygenates to reduce summer ozone and winter carbon monoxide levels in nonattainment areas. Much of the MTBE is used in reformulated gasoline (RFG) program areas (fig. 1) where the concentration of MTBE in gasoline is 11 percent by volume and is used year round. When

used in oxygenated gasoline (OXY) areas (figs. 1 and 2), the concentration of MTBE is as much as 15 percent by volume during the winter months. However, ethanol is the more common oxygenate used in OXY gasoline. The release of MTBE to ground and surface water may come largely from point sources, such as leaks or spills, especially during the distribution, storage, and use of the blended gasoline (Zogorski and others, 1997).

The chemical characteristics of MTBE, such as high solubility in water, low Henry's Law constant, low soil-sorption properties, and unresponsiveness to treatment in ground water, may result in extensive contamination of some private and public drinking-water sources. MTBE also is a possible human carcinogen. The U.S. Environmental Protection Agency (USEPA) has issued a drinking-water advisory of concentrations in the range of 20 to 40 $\mu\text{g/L}$ (micrograms per liter) to avert unpleasant taste and odor effects (U.S. Environmental Protection Agency, 1997a). The State of California has issued a taste and odor limit of 5 $\mu\text{g/L}$ and a maximum contamination level (MCL) of 13 $\mu\text{g/L}$ (California Department of Health Services, 2001). Currently (2001), a national MCL for MTBE has not yet been issued by the USEPA.

Because of the chemical characteristics of MTBE and its presence in source water, some cities, especially in California, have already lost a substantial number of drinking-water sources. Santa Monica, where 75 percent of the drinking-water wells are unusable due to MTBE (City of Santa Monica, 1999), South Lake Tahoe, where one-third of the city's 34 drinking-water wells have been lost to MTBE contamination (Bourelle, 1998), Los Angeles, San Francisco, Santa Clara Valley, and Sacramento, all have wells affected by MTBE (California Department of Health Services, 2001). Other cities with affected drinking-water supplies include LaCrosse, Kansas (Hatten, 2000), and Windham, Maine (State of Maine, 1998), where officials have taken steps to remediate the problem or remove the wells from service. Because the extent of MTBE occurrence in the Nation's drinking-water supplies has not been adequately described due to limited data, an Interagency Assessment of Oxygenated Fuels (Zogorski and others, 1997) recommended that additional data be collected.

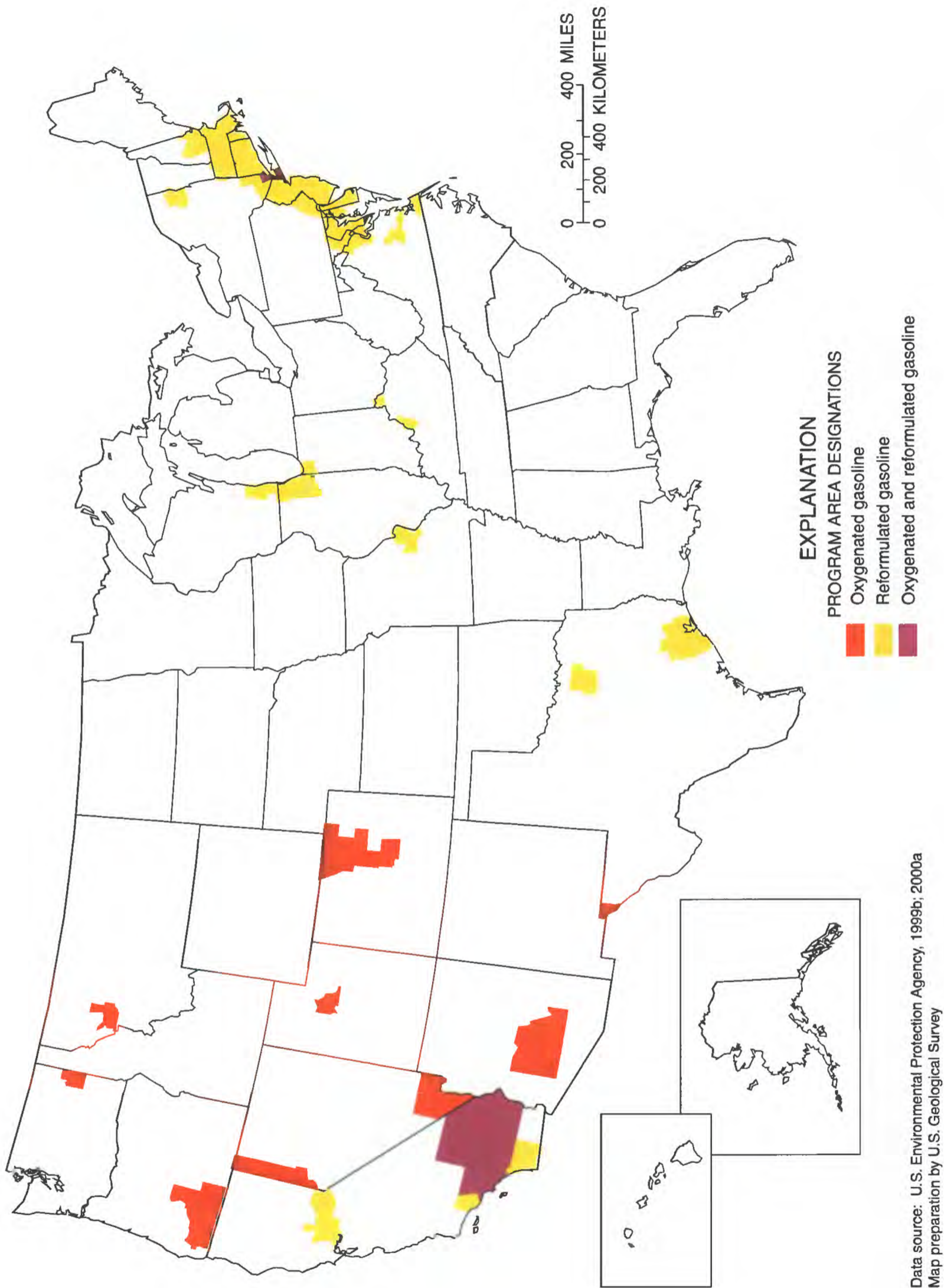
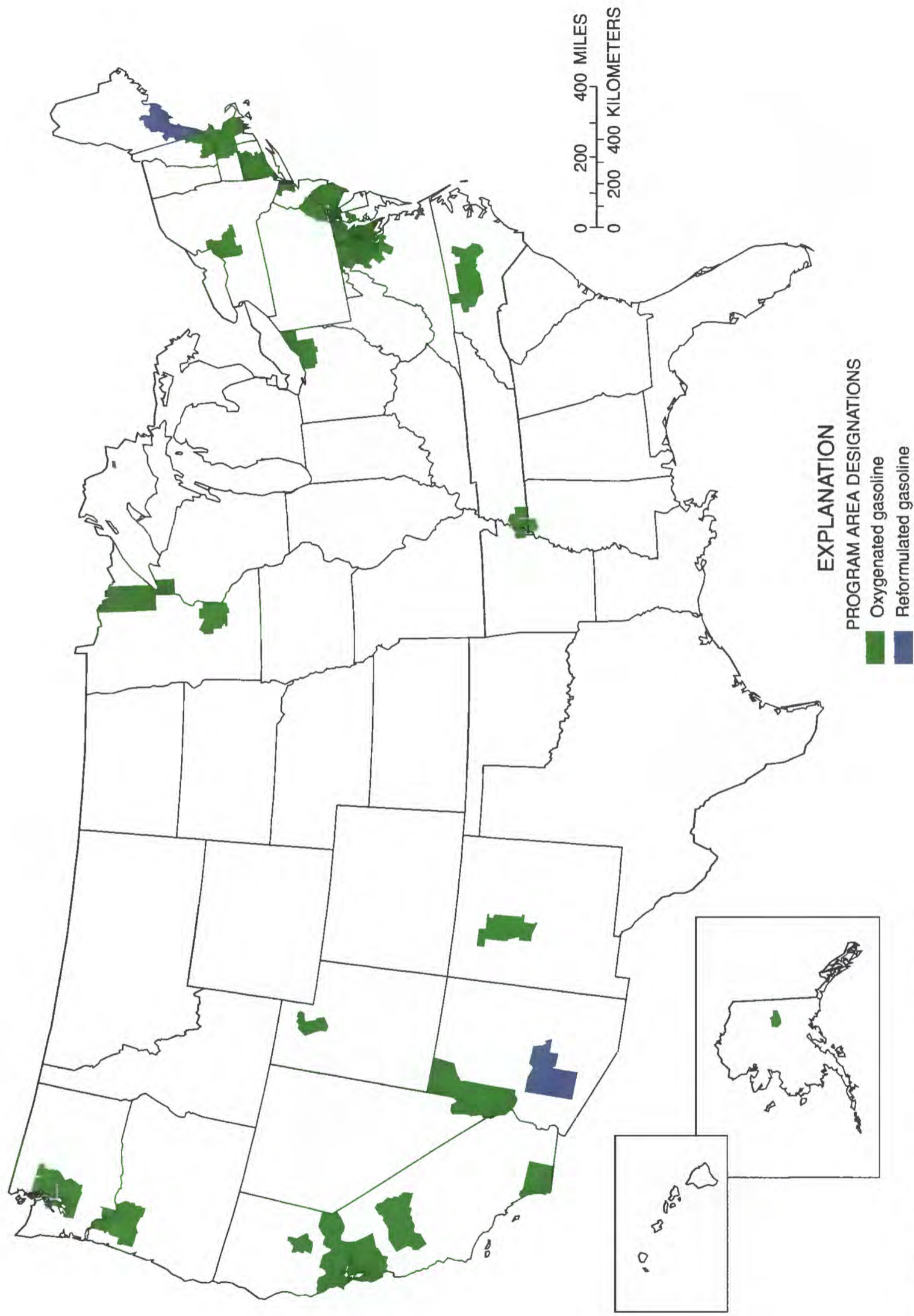


Figure 1. Location of current (2000) Federal oxygenated and reformulated gasoline program areas.



Data source: U.S. Environmental Protection Agency, 1999b; 2000a
 Map preparation by U.S. Geological Survey

Figure 2. Location of former Federal oxygenated and reformulated gasoline program areas.

Approximately 180,000 public water systems (PWSs) provide drinking water, at least some of the time, to about 252 million people in the 50 States, the District of Columbia, Native American Lands, and Puerto Rico (U.S. Environmental Protection Agency, 1997b); however, only about 54,300 of the PWSs are considered community water systems (CWSs) that supply water to the same population year round.

Although non-transient non-community water systems (NTNCWSs), which include schools, factories, and hospitals, can contribute substantially to an individual's daily water intake, the population served by NTNCWSs (about 6 million) is relatively small in comparison to the population served by CWSs. Solley and others (1998) reported that the number of people using public-supplied water year round is expected to increase; therefore, the potential number of people being served by CWSs that contain MTBE in the source waters could currently be substantial, and increase in the future. The U.S. Geological Survey (USGS) National Water Quality Assessment Program (NAWQA) National Volatile Organic Compound (VOC) Synthesis Team, in collaboration with the Metropolitan Water District of Southern California (MWDSC) in LaVerne, California, and the Oregon Graduate Institute of Science and Technology (OGI) in Beaverton, Oregon, is to design and conduct a nationwide survey to determine the occurrence and distribution of MTBE and other VOCs in ground and surface water that serve as public drinking-water supplies. The investigation is sponsored by the American Water Works Association Research Foundation. This survey will provide a basis for determining the extent of MTBE and other VOC contamination throughout the United States by sampling a large enough population of CWSs to allow statistical analysis with a high degree of confidence from the findings. In addition, the survey will provide information about the frequency of detection, concentration, and temporal variability of MTBE and other gasoline oxygenates, their degradation products, and other VOCs in source water with suspected or known MTBE contamination. The information from this survey also will help accomplish the goals of the USGS VOC National Synthesis by determining the occurrence and distribution of VOCs in ground and surface water that serve as public drinking-water supplies.

Purpose and Scope

This report describes the design of a national survey of MTBE in public-supply drinking-water sources. The survey consists of two independent stages designed to provide representative sampling of all CWSs in the United States (Random Source-Water Survey) and to improve understanding of the temporal variability of MTBE in selected water sources (Focused Source-Water Survey). The Random Source-Water Survey will provide representative information on the frequency of detection, concentration, and distribution of MTBE, other gasoline oxygenates, and other VOCs in 1,000 untreated, ground- and surface-water sources of drinking water used by CWSs in the United States. The Focused Source-Water Survey will provide an improved understanding of the frequency of detection, concentration, and temporal variability of MTBE, other gasoline oxygenates, their degradation products, and other VOCs in about 120 sources of untreated water with suspected or known MTBE contamination. The focused design will consider, in part, factors that appear to be related to frequent detection of MTBE and other VOCs, when selecting CWSs for sampling. Then samples will be collected to better characterize the variability in the detection and concentrations of a wide range of VOCs and oxygenate byproducts.

This report also describes the logic and statistical analysis used to design a stratified selection scheme to minimize bias of CWSs for the Random Source-Water Survey. Similarly, justification for selection of CWSs for the Focused Source-Water Survey also is provided.

Acknowledgments

The authors would like to thank George D. Casey for his efforts in compiling the information on the CWSs to be used in the Random Source-Water Survey. The authors also thank Lori Apodaca, Joyce Williamson, and Mike Focazio, all of the USGS for their technical review of this report.

SURVEY DESIGN

Two different but complimentary survey designs are being used. For the Random Source-Water Survey, statistical analysis will be required to ensure an unbiased distribution of CWSs by State, source type (ground water or surface water), and population served.

The Focused Source-Water Survey, which uses a fixed-interval sampling regime, also is being conducted in two parts. Samples will be collected to characterize possible temporal VOC variations by sampling wells twice in the year, reservoirs and lakes quarterly, and rivers eight times in the year. In the first part of the Focused Source-Water Survey, metropolitan areas with CWSs that serve large populations (greater than 50,000) and are in RFG (high MTBE-use) areas where MTBE is suspected of contaminating drinking-water sources, will be solicited for participation. Other CWS sources suspected of having concentrations of MTBE will be selected by using the following criteria: sources being near leaking underground storage tanks (LUST), in or near former RFG areas, and high watercraft use on surface-water sources. Second, the Focused Source-Water Survey will build upon data from the results of the Random Survey as CWSs with known concentrations of MTBE will be selected for inclusion in the Focused Survey. Selection of additional CWSs with known concentrations of MTBE for inclusion in the Focused Survey will be made through various sources including State environmental and drinking-water reports, discussions with State officials, and other sources.

Sample Collection/Analysis and Quality Assurance/Quality Control

All samples for both the Random and Focused Source-Water Surveys will be analyzed for MTBE, three other ether gasoline oxygenates, and 62 other VOCs (table 1) at the MWDSC laboratory in LaVerne, California, using the USEPA approved method 524.2 (U.S. Environmental Protection Agency, 1992). Environmental samples and field blanks for the Random Source-Water Survey will be collected by CWS personnel. Samples for the Random Source-Water Survey will be collected once by each participating CWS. Instructions for collecting the VOC samples will be provided by MWDSC to CWS personnel, with emphasis on collecting a raw (untreated) water sample. Two drops of 50-percent dilute hydrochloric acid will be added to 40-mL (milliliter) baked-glass VOC vials prior to shipment to the field. Commercially produced blank water will be randomly tested at the MWDSC laboratory to ensure purity and sent to the CWSs to be used for collection of field blanks. Every environmental sample submitted to the MWDSC laboratory will be accompanied by a field blank. Field blanks will be collected and processed in the same location as the

environmental sample, thereby exposing the blank water to sampling conditions. Field blanks also will be preserved with one or two drops of 50-percent dilute hydrochloric acid. The field blank will be analyzed only if VOCs are detected in the corresponding environmental sample. Travel blanks, filled with commercially produced blank water and sealed at the MWDSC, also will accompany all environmental samples. Travel blanks will never be uncapped by the samplers but will be analyzed if VOCs are detected in the environmental sample.

Samples for the Focused Source-Water Survey will be collected by USGS personnel using USGS protocols. Ground-water samples will be collected from water-supply wells as described by Koterba and others (1995). Quality-control sampling will include equipment blanks (20 percent of the samples) and duplicates (10 percent of the samples). Also, ground- and surface-water quality-control samples will include field blanks at 100 percent of the sites. Field and equipment blanks will be collected with commercially produced VOC-free blank water tested and shipped by MWDSC. Surface-water samples will be collected within 5 feet of the surface using a VOC hand-sampler as described by Shelton (1997) and Halde and others (1998). Surface-water quality-control samples, primarily equipment blanks, will be collected as described by Shelton (1997).

Focused Source-Water Survey samples will be collected at the following intervals: wells biannually, reservoirs quarterly, and rivers eight times. Ground-water field-equipment blanks will not be collected because permanently installed pumps will be used to collect the samples. Because Focused Survey samples will be collected at the same site more than one time, surface-water equipment blanks will be collected at approximately 70 percent of the sites. Duplicate samples will be collected when VOCs are known to occur on the basis of previous sampling at the sites, and will be distributed evenly among the ground-water and surface-water sites. Physical properties, including specific conductance, pH, air and water temperature, and dissolved oxygen, will be measured onsite prior to sampling ground water to ensure that representative aquifer water is being sampled. Similarly, physical properties will be measured prior to sampling surface water, to document local sampling conditions. All environmental samples, duplicates, and blanks will be preserved in the field with purchased pre-diluted 1:1 hydrochloric acid.

Table 1. Volatile organic compounds analyzed for Random and Focused Source-Water Surveys

[MDL, method detection limit; MRL, minimum reporting level; MCL, Maximum Contaminant Level; HA, health advisory; DWCCCL, U.S. Environmental Protection Agency Drinking-Water Candidate Contaminant List; µg/L, micrograms per liter; --, not applicable]

Compound	MDL (µg/L)	MRL (µg/L)	MCL ¹ (µg/L)	HA ¹ (µg/L)	DWCCCL ²
Gasoline Oxygenates					
Methyl <i>tert</i> -butyl ether (MTBE)	0.039	0.2	--	20-40	Yes
Methyl <i>tert</i> -amyl ether	.025	.2	--	--	--
Ethyl <i>tert</i> -butyl ether	.034	.2	--	--	--
Diisopropyl ether	.073	.2	--	--	--
Other Volatile Organic Compounds					
Bromobenzene	.029	.2	--	--	Yes
Bromomethane	.084	.2	--	10	Yes
1,1-Dichloroethane	.036	.2	--	--	Yes
1,3-Dichloropropane	.029	.2	--	--	Yes
2,2-Dichloropropane	.056	.2	--	--	Yes
1,1-Dichloropropene	.060	.2	--	--	Yes
<i>cis</i> -1,3-Dichloropropene	.024	.2	--	--	Yes
<i>trans</i> -1,3-Dichloropropene	.026	.2	--	--	Yes
Hexachlorobutadiene	.057	.2	--	1	Yes
4-Isopropyltoluene	.037	.2	--	--	Yes
Napthalene	.055	.2	--	--	Yes
1,1,2,2-Tetrachloroethane	.026	.2	--	--	Yes
1,2,4-Trimethylbenzene	.022	.2	--	--	Yes
Acrylonitrile	.098	.2	--	--	--
Benzene	.029	.2	5	--	--
Bromochloromethane	.036	.2	--	90	--
Bromodichloromethane	.018	.2	(³)	--	--
Bromoform	.022	.2	(³)	--	--
2-Butanone	.645	2	--	--	--
<i>sec</i> -Butylbenzene	.044	.2	--	--	--
<i>tert</i> -Butylbenzene	.037	.2	--	--	--
<i>n</i> -Butylbenzene	.047	.2	--	--	--
Carbon tetrachloride	.049	.2	5	--	--
Chlorobenzene	.032	.2	100	100	--
Chloroethane	.230	.2	--	--	--
Chloroform	.126	.2	(³)	--	--
Chloromethane	.150	.2	--	3	--
2-Chlorotoluene	.042	.2	--	100	--
4-Chlorotoluene	.040	.2	--	100	--
Dibromochloromethane	.133	.2	(³)	60	--

Table 1. Volatile organic compounds analyzed for Random and Focused Source-Water Surveys—Continued

[MDL, method detection limit; MRL, minimum reporting level; MCL, Maximum Contaminant Level; HA, health advisory; DWCCCL, U.S. Environmental Protection Agency Drinking-Water Candidate Contaminant List; µg/L, micrograms per liter; --, not applicable]

Compound	MDL (µg/L)	MRL (µg/L)	MCL ¹ (µg/L)	HA ¹ (µg/L)	DWCCCL ²
Other Volatile Organic Compounds—Continued					
1,2-Dibromoethane	0.133	0.2	0.05	--	--
Dibromomethane	.035	.2	--	--	--
1,2-Dichlorobenzene	.031	.2	600	600	--
1,3-Dichlorobenzene	.045	.2	--	600	--
1,4-Dichlorobenzene	.033	.2	75	75	--
Dichlorodifluoromethane	.190	.2	--	1,000	--
1,2-Dichloroethane	.055	.2	5	--	--
1,1-Dichloroethene	.130	.2	7	7	--
<i>cis</i> -1,2-Dichloroethene	.130	.2	70	70	--
<i>trans</i> -1,2-Dichloroethene	.200	.2	100	100	--
1,2-Dichloropropane	.053	.2	5	--	--
Ethylbenzene	.032	.2	700	700	--
1,1,1,2,2,2-Hexachloroethane	.086	.2	--	1	--
Isopropylbenzene	.074	.2	--	--	--
Methylene chloride	.099	.2	5	--	--
n-Propylbenzene	.260	.2	--	--	--
Styrene	.031	.2	100	100	--
1,1,1,2-Tetrachloroethane	.048	.2	--	70	--
Tetrachloroethene	.047	.2	5	--	--
Toluene	.047	.2	1,000	1,000	--
1,2,3-Trichlorobenzene	.047	.2	--	--	--
1,2,4-Trichlorobenzene	.043	.2	70	10	--
1,1,1-Trichloroethane	.043	.2	200	200	--
1,1,2-Trichloroethane	.043	.2	5	3	--
Trichloroethene	.045	.2	5	--	--
Trichlorofluoromethane	.059	.2	--	2,000	--
1,2,3-Trichloropropane	.072	.2	--	40	--
1,1,2-Trichloro-1,2,2-trifluoroethane	.065	.2	--	--	--
1,3,5-Trimethylbenzene	.035	.2	--	--	--
Vinyl chloride	.120	.2	2	--	--
m,p-Xylene	.038	.2	10,000	10,000	--
o-Xylene	.038	.2	10,000	10,000	--

¹U.S. Environmental Protection Agency, 2000b.²U.S. Environmental Protection Agency, 1998a.³Total for trihalomethanes cannot exceed 80 µg/L.

Approximately one-half of the samples collected as part of the Focused Source-Water Survey will be analyzed for oxygenate by-products using an analytical method developed by the OGI (Church and others, 1997) and then modified (Wentai Luo, L.M. Isabelle, and J.F. Pankow, Oregon Graduate Institute, written commun., 2001). This method has a rapid and sensitive detection of *tert*-butyl alcohol (TBA) and other likely products of MTBE degradation including *tert*-butyl formate (TBF), methyl acetate, isopropanol, and acetone at the microgram per liter concentration level or lower (Wentai Luo, L.M. Isabelle, and J.F. Pankow, Oregon Graduate Institute, written commun., 2001). The OGI laboratory is one of the few laboratories in the country that has a rapid and sensitive method (low reporting limit) for analyzing oxygenate degradation products. Samples and blanks to be analyzed by the OGI laboratory will be collected using the same USGS field protocols; the only variation will be no addition of 1:1 hydrochloric acid. Samples will be chilled only to prevent acid corrosion of the mass spectrometer source and damage to the gas chromatograph's columns (Wentai Luo, L.M. Isabelle, and J.F. Pankow, Oregon Graduate Institute, written commun., 2001). Samples will be analyzed for oxygenate degradation products when MTBE or other fuel oxygenates are likely or known to be present in the sample.

Random Source-Water Survey

The Random Source-Water Survey will determine the frequency of detection and the range in concentrations of MTBE, three other ether gasoline oxygenates, and 62 other VOCs (table 1) in drinking-water sources through a representative random sampling of 1,000 CWSs. Information on the frequency and concentration of MTBE and other VOCs in drinking-water sources for the 1,000 CWSs will be determined through samples collected using a statistically stratified design.

The results of the VOC analyses will have a binomial distribution because a compound either will be detected or will not be detected, or does or does not exceed a specified concentration threshold such as a method reporting level. The number of samples required to provide a specified confidence interval for the unknown probability (p) of a VOC being detected (or exceeding some concentration threshold) with an allowable error (d) of “+ or - d ” can be determined from the binomial distribution (Iman and Conover,

1983). With 1,000 samples, p can be determined to be within ± 3.1 percent at the 95-percent confidence level. Previous USEPA national surveys of VOCs had similar or smaller sample sizes (Westrick, 1990). Also, estimates of the number of samples that could physically be processed monthly by the MWDSC laboratory, in addition to its normal regulatory sample load, will be considered to ensure that the laboratory can process the additional samples from this survey.

Of the 54,000 CWSs in the United States, only about 11 percent rely on surface-water sources (U.S. Environmental Protection Agency, 1998b). However, in 1998, these surface-water sources supplied nearly 168 million people or two-thirds of the total population served by CWSs. Most CWSs (about 89 percent) are exclusively or primarily ground-water supplied, but they collectively served just one-third of the total population, or about 84 million people in 1998 (U.S. Environmental Protection Agency, 1998b). Thus, a sample size of 1,000 CWSs selected exclusively on the basis of distribution by source water would result in about 89 percent of the systems sampled in the Random Source-Water Survey being ground-water sources. This would strongly bias the results of the Random Source-Water Survey towards small systems in rural parts of the country. Conversely, if the design considered only the population served by CWSs, two-thirds of the sampled CWSs would be surface-water supplied, and the results of the survey again would be biased. A more balanced design for the Random Source-Water Survey consequently will consider both factors—source of water and population served—as stratification factors.

Data on the number of CWSs and the population served by active CWSs were obtained from the USEPA's Safe Drinking Water Information System (SDWIS) on November 5, 1998. These data indicate that there were 54,305 active CWSs serving 251,659,380 people in the United States, Native American Lands, and Puerto Rico on that date. According to the SDWIS data base, however, 7,345 systems purchase 100 percent of the water they distribute from other CWSs. Systems that purchase 100 percent of their water supplies do not have ground- or surface-water sources that could be sampled for this survey. Therefore, the 7,345 purchased-water CWSs will be excluded from the count of systems, but not from data pertaining to population served, used to design the Random Source-Water Survey (table 2).

Table 2. Number of self-supplied community water systems and number of people served, by source of water and size of system, November 5, 1998

[Data from U.S. Environmental Protection Agency's Safe Drinking Water Information System (URL <http://www.epa.gov/enviro/html/sdwis/>). CWS, community water system]

CWS-size category ¹	Ground water		Surface water	
	Number of systems	Number of people served	Number of systems	Number of people served
Very small	28,324	4,625,130	1,228	616,012
Small	9,775	14,178,037	1,562	5,739,217
Medium	2,399	14,219,831	971	11,045,463
Large	1,194	25,342,137	928	36,525,585
Very large	182	25,696,338	397	113,671,630
Total	41,874	84,061,473	5,086	167,597,907

¹Very small; serving less than 500 people;
 Small, serving 501 to 3,300 people;
 Medium, serving 3,301 to 10,000 people;
 Large, serving 10,001 to 50,000 people;
 Very large, serving more than 50,000 people.

The range in population served by CWS will be divided into five CWS-size categories in this survey. Generally, they will be the same categories that are used by the USEPA when presenting information on the occurrence of contaminants in drinking water (U.S. Environmental Protection Agency, 1993) with one difference—the category that defines the very large CWSs will include all systems that serve 50,000 or more people rather than the 100,000 or more people used by the USEPA. This change is intended to include more of the larger systems, and a larger portion of the population in the random design. The five CWS-size categories used in the Random Source-Water Survey are given in table 2.

The design of the Random Source-Water Survey will distribute the total number of samples (1,000) among 10 source-size categories (five for ground water, five for surface water) relative to the national distribution of total number of self-supplied systems and the total number of people served by CWSs within each category (tables 2 and 3). The percentage of the total number of CWSs within each source-size category (A) and the percentage of the total population served by all CWSs within that particular source-size category (B) will be summed and divided by 2 (C)

(table 3). The number of CWSs to be sampled per category (D) will be the number obtained (C) multiplied by 10. Consequently, the distribution of CWSs sampled will include 311 very small ground-water systems reflecting the prevalence of such systems in the national distribution, but also will include 230 very large surface-water systems—reflecting the large percentage of the population served by those systems (table 3).

The Random Source-Water Survey will sample 613 ground-water-supplied systems and 387 surface-water-supplied systems. Using the mean population served by each CWS within the 10 source-size categories, a survey of 1,000 CWSs would provide information on VOC concentrations in source water used by an estimated 80 million people, or about 31 percent of the total population served by CWSs as of November 5, 1998. Using source-water type alone in the design, information pertinent to only about 2 million people would be included in the survey. When the Random Source-Water Survey selection process has been completed, information specific to each participating CWS can be summarized to provide an actual determination of the total population served by the selected systems and the percentage of all CWS customers represented.

Table 3. Number of community water systems to be sampled during Random Source-Water Survey on basis of mean percentage of total number of systems and total number of people served by size category and source of water

[GW, ground water; SW, surface water; VSM, very small; SM, small; MED, medium; LRG, large; VLRG, very large; CWSs, community water systems]

Source-size category	(A) Percentage of total number of systems	(B) Percentage of total number of people served	(C) (A+B)/2	(D) Number of CWSs to be sampled by source and size
GW-VSM	60.3	1.84	31.1	311
GW-SM	20.8	5.63	13.2	132
GW-MED	5.11	5.65	5.38	54
GW-LRG	2.54	10.1	6.32	63
GW-VLRG	.39	10.2	5.30	53
Ground-water subtotal	89.1	33.4	61.3	613
SW-VSM	2.64	.24	1.44	14
SW-SM	3.33	2.28	2.80	28
SW-MED	2.07	4.39	3.23	32
SW-LRG	1.98	14.5	8.24	83
SW-VLRG	.85	45.2	23.0	230
Surface-water subtotal	10.9	66.6	38.7	387
Total	100.0	100.0	100.0	1,000

Allocation of Samples by State

In an extension of the overall design of the Random Source-Water Survey, a stratified random selection of CWSs will be conducted on the basis of the number of systems and population served within each of 52 geographic entities—the 50 States, Native American Lands, and Puerto Rico. The stratified random selection will be made from lists of CWSs in each of the 52 geographic entities to provide a more representative distribution of participating CWSs than might be obtained from a simple random selection from the total, national population of CWSs in each category.

Similar to the overall design process, an average of the percentage of the number of CWSs and the percentage of the population served within each source-size category will be calculated for each State, and for Native American Lands and Puerto Rico. This mean percentage for each of the 52 geographic entities will be multiplied by the total number of CWSs to be sampled from each category in the overall design (table 3). For example, in California there were 1,963 ground-water-supplied, very small CWSs that collectively supply 269,727 people as of November 5, 1998. Consequently, California had 6.9 percent of the 28,324 CWSs and 5.8 percent of the 4.6 million people served

by CWSs in the very small category (table 2).

Averaging these two values, California would have 6.4 percent of the 311 ground-water-supplied, very small CWSs to be sampled in the Random Source-Water Survey, or (with rounding) 20 unbiasedly selected CWSs from this source-size category.

Table 4 lists the number of participating CWSs from each geographic entity for each of the 10 source-size categories. Selections will be made from randomized lists of active, self-supplied water utilities obtained from the SDWIS data base on November 5, 1998, until the requisite number of systems is obtained for each source-size category in each State, Native American Lands, and Puerto Rico.

Lists of CWSs for each source-size category and geographic entity where one or more participating CWSs will be needed (table 4) will be randomized using the uniform random distribution method in Microsoft Excel 5.0 (Microsoft, Inc., Seattle, Washington). Random numbers between 0 and 1.0 will be generated for each CWS and sorted from lowest to highest. Identification of participating suppliers will be made by contacting each CWS in sequence (from the list) to solicit their participation in the survey. This process will be followed until the requisite number of systems (table 4) is achieved.

Table 4. Community water systems to be sampled during the Random Source-Water Survey by source-size category and by State

[GW, ground water; SW, surface water; VSM, very small; SM, small; MED, medium; LRG, large; VLRG, very large]

State ¹ or other entity	Source-size category										Total
	GW-VSM	GW-SM	GW-MED	GW-LRG	GW-VLRG	SW-VSM	SW-SM	SW-MED	SW-LRG	SW-VLRG	
AK	4	1	0	0	0	1	0	0	0	1	7
AL	0	2	2	1	0	0	0	1	3	5	14
AR	2	2	1	0	0	0	1	1	1	1	9
AZ	5	2	1	2	1	0	0	0	0	6	17
CA	20	5	3	7	11	2	2	2	5	30	87
CO	5	1	0	0	0	1	1	1	2	6	17
CT	5	1	0	0	0	0	0	0	2	5	13
DE	2	1	0	0	0	0	0	0	0	1	4
FL	13	6	3	7	17	0	0	0	1	3	50
GA	12	3	1	1	1	0	1	1	3	8	31
HI	0	1	0	0	1	0	0	0	0	0	2
IA	7	4	1	1	1	0	0	0	0	2	16
ID	5	1	1	1	0	1	0	0	0	1	10
IL	7	5	2	2	1	0	1	1	3	8	30
IN	4	4	2	2	1	0	0	1	1	4	19
KS	4	3	0	1	0	0	1	1	1	3	14
KY	1	0	0	0	0	0	1	2	5	2	11
LA	8	5	3	2	2	0	0	1	1	5	27
MA	2	1	2	3	1	0	0	1	4	8	22
MD	4	1	1	1	0	0	0	0	1	5	13
ME	2	1	0	0	0	0	1	0	1	0	5
MI	9	4	1	1	1	0	0	1	2	4	23
MN	6	4	1	3	0	0	0	0	1	2	17
MO	8	4	2	1	1	0	1	1	1	4	23
MS	5	9	3	2	0	0	0	0	0	0	19
MT	5	1	0	0	0	0	0	0	0	1	7
NC	16	3	1	1	0	0	1	2	4	7	35
ND	1	1	0	0	0	0	0	0	1	0	3
NE	5	2	1	1	0	0	0	0	0	1	10
NH	5	1	0	0	0	0	0	0	1	1	8
NJ	3	2	2	4	1	0	0	0	1	8	21
NM	5	1	1	1	1	0	0	0	0	0	9
NV	2	1	0	0	0	0	0	0	0	1	4
NY	15	4	1	3	4	1	2	2	4	16	52

Table 4. Community water systems to be sampled during the Random Source-Water Survey by source-size category and by State—Continued

[GW, ground water; SW, surface water; VSM, very small; SM, small; MED, medium; LRG, large; VLRG, very large]

State ¹ or other entity	Source-size category										Total
	GW-VSM	GW-SM	GW-MED	GW-LRG	GW-VLRG	SW-VSM	SW-SM	SW-MED	SW-LRG	SW-VLRG	
OH	7	4	2	3	2	0	1	1	4	10	34
OK	3	2	1	1	0	1	2	2	2	4	18
OR	6	1	0	1	0	1	1	1	2	2	15
PA	14	5	2	1	0	1	1	2	6	15	47
RI	0	0	0	0	0	0	0	0	0	1	1
SC	4	1	1	0	0	0	0	0	2	3	11
SD	2	1	0	0	0	0	0	0	0	1	4
TN	1	1	1	1	1	0	1	2	4	4	16
TX	24	14	6	3	3	1	2	2	5	17	77
UT	3	1	1	1	0	0	0	0	0	4	10
VA	11	2	0	0	0	0	1	1	2	6	23
VT	3	1	0	0	0	0	1	0	0	0	5
WA	17	4	1	2	1	1	1	0	1	2	30
WI	7	4	2	1	1	0	0	0	1	3	19
WV	2	1	0	0	0	0	2	1	1	1	8
WY	2	0	0	0	0	0	0	0	0	0	2
NA ²	6	2	0	0	0	1	0	0	0	0	9
TE ³	2	1	1	1	0	2	2	1	4	8	22
Total	311	132	54	63	53	14	28	32	83	230	1,000

¹Postal Service State abbreviation.

²Native American Lands.

³Puerto Rico.

Temporal Distribution of Samples

Because the Random Source-Water Survey will be implemented over a 15-month period, the temporal distribution of CWS sample collection also will be distributed to prevent any seasonal bias in the data. Sampling of source water at selected CWSs is planned to occur from April 1999 through June 2000. Although the sampling will take place over a 64-week period, the number of samples collected weekly will provide for an even distribution over a 52-week calendar year. Accomplishing that distribution requires that about one-half of the number of weekly samples collected

during the middle 40 weeks of the survey be collected during the initial and final 12 weeks. Consequently, 10 samples per week will be collected during weeks 1 through 12 and weeks 53 through 64, whereas 19 samples per week will be collected during weeks 13 through 52.

A spatial distribution of CWSs to be sampled during any specific week over the 64-week duration of the Random Source-Water Survey will be needed to prevent any regional bias in the temporal sample distribution. Generic identification of the 1,000 CWSs sampled will allow a pre-selection and temporal randomization of the CWS sampling sequence.

Information on the source-size category, State, and number of CWSs from table 4 will be combined to create a generic identifier for each of the planned 1,000 CWSs. For example, table 4 indicates that there will be four ground-water-supplied, very small CWSs sampled from Alaska; therefore, four of the generic identifiers will be “GW_VSM.AK1,” “GW_VSM.AK2,” “GW_VSM.AK3,” and “GW_VSM.AK4.” Similar identifiers will be created for the other 996 CWSs to be included in the Random Source-Water Survey as indicated in table 4. The generic identifiers serve as “place holders” in the random temporal distribution design until actual selection of the participating CWSs is complete.

The list of the 1,000 generic identifiers will be randomized using the uniform random distribution method in Microsoft Excel 5.0 (Microsoft, Inc., Seattle, Washington). Random numbers between 0 and 1.0 will be generated for each CWS and sorted from lowest to highest. Generic identifiers then will be apportioned among the 64-week sampling sequence according to the sorted random numbers and the number of samples allocated to each week (either 10 or 19). Table 5 gives the results of this procedure for the first and last weeks of the Random Source-Water Survey sampling sequence when 10 samples will be collected during each week.

Table 5. Community water systems to be sampled during first and last weeks of Random Source-Water Survey

[CWS, community water system; GW, ground water; SW, surface water; VSM, very small; SM, small; MED, medium; LRG, large; VLRG, very large]

Sample sequence	Random number	Sample week	Generic CWS identifier	State ¹
1	0.002807703	Week 1	GW_SM.IN1	IN
2	0.004974517	Week 1	GW_LRG.OH1	OH
3	0.005157628	Week 1	GW_SM.MO1	MO
4	0.005920591	Week 1	GW_VSM.WI1	WI
5	0.008178961	Week 1	GW_VSM.GA1	GA
6	0.008575701	Week 1	SW_VLRG.CA1	CA
7	0.014191107	Week 1	SW_VSM.NA1	NA
8	0.014221625	Week 1	GW_VLRG.FL1	FL
9	0.014252144	Week 1	SW_VLRG.MO1	MO
10	0.014496292	Week 1	GW_LRG.CA1	CA
991	0.990447707	Week 64	GW_VLRG.CA11	CA
992	0.991241188	Week 64	GW_LRG.MA3	MA
993	0.992522965	Week 64	SW_VLRG.MI4	MI
994	0.993255409	Week 64	GW_VSM.NA6	NA
995	0.993774224	Week 64	SW_VLRG.CA30	CA
996	0.994232002	Week 64	SW_LRG.TE4	TE
997	0.995330668	Week 64	GW_VSM.MN6	MN
998	0.997711112	Week 64	GW_SM.FL6	FL
999	0.998168889	Week 64	GW_VSM.WA17	WA
1,000	0.998718223	Week 64	GW_VSM.VA11	VA

¹Postal Service State abbreviation.

Table 6 includes information used to evaluate how well the random temporal sample distribution allocates samples from various parts of the Nation and its Territories over a 12-month “calendar year.” The 50 States, Native American Lands, and Puerto Rico will be assigned to eight “regions,” and the total number of samples to be collected within each region during each calendar month (assuming that week 1 of the survey will be May 2-8, 1999, and week 64 will be July 16-22,

2000) will be counted. For most regions, the month-to-month variability in the number of samples collected will be small, and the coefficient of variation for all regions except “other” will be less than 0.5 and mostly less than 0.3. The “other” region will have the fewest samples (40), but it also will include geographic entities that are not in similar geographic or climatic regions (Alaska, Hawaii, Native American Lands, and Puerto Rico).

Table 6. Community water systems to be sampled during Random Source-Water Survey over a 12-month calendar year in eight regions of the United States

Region ¹	Jan	Feb	Mar	Apr	May	June	July	Aug	Sep	Oct	Nov	Dec	Total
Northeast and Mid-Atlantic	15	21	22	8	21	23	15	17	22	13	16	21	214
Southeast	10	11	20	13	15	8	13	11	18	11	11	16	157
Ohio Valley	12	17	7	10	13	7	10	10	11	12	8	8	125
Upper Midwest	6	7	7	12	8	9	17	6	6	9	9	10	106
South Central	11	11	11	14	10	16	19	9	13	7	10	19	150
Southwest	13	5	17	13	7	11	12	12	16	11	15	12	144
Northwest	3	3	7	5	4	4	4	8	6	7	7	6	64
Other	6	1	4	5	2	2	5	3	3	6	0	3	40
Total	76	76	95	80	80	80	95	76	95	76	76	95	1,000

¹Regions (Postal Service State abbreviation):

Northeast and Mid-Atlantic: CT, DE, MA, MD, ME, NH, NJ, NY, PA, RI, VA, and VT;

Southeast: AL, FL, GA, NC, SC, and TN;

Ohio Valley: IL, IN, KY, MI, OH, and WV;

Upper Midwest: IA, KS, MN, MO, ND, NE, SD, and WI;

South Central: AR, LA, MS, OK, and TX;

Southwest: AZ, CA, CO, NM, NV, and UT;

Northwest: ID, OR, MT, WA, and WY;

Other: AK, HI, Native American Lands, and Puerto Rico.

Ancillary Information Collection

Ancillary information will enable statistical analysis of possible relations between the occurrence and distribution of MTBE or other VOCs in source-water samples collected for the Random Source-Water Survey and various natural or anthropogenic factors. Ancillary information will include location (latitude and longitude) of the sources sampled (well head or intakes); actual population served by the source; source characteristics (for example, well depth, yield, aquifer type, surface-water type and size, intake specifics, and previous water-quality problems); MTBE and other fuel-oxygenate use areas; land use; population density; and known or potential VOC point-source locations (toxic release inventory sites, LUSTs, and sites

regulated by the Resource Conservation and Recovery Act or Comprehensive Environmental Response and Compensation and Liability Act) in the vicinity of sampled CWS sources. This information will be obtained from available data bases or collected directly from participating CWSs.

Information on the precise location of CWS sources often is missing from the SDWIS data base and will be collected from the participating CWSs. National geospatial data on land use, population density, and point-source locations are available and will be utilized to provide a consistent coverage for all participating CWSs. Information on MTBE or other fuel-oxygenate use will be compiled from USEPA documentation and industry surveys.

A short questionnaire will be filled out during an initial telephone interview with CWS staff when they have agreed to participate in the Random Source-Water Survey. The questionnaire will be used to verify basic information obtained from the SDWIS data base for the selected utility, ascertain additional information on the source water to be sampled, and identify the persons and the means for further contact.

A written questionnaire (Appendix A) will be included with the sampling supplies sent to participating CWSs to record additional ancillary information about the source water, intake location, filtration and treatment, distribution area, actual population served, and quantity of water delivered by suppliers. The written questionnaire also will solicit information specific to ground-water sources (well characteristics, aquifer type, and any known or potential VOC point-source locations) or surface-water sources (watershed protection, watercraft use). In addition, latitude and longitude information will be collected from each utility for each sampled source (intake or wellhead). If latitude and longitude are not available, the CWSs will be asked to identify the location of sources (wellhead or intake) on a topographic map, from which USGS personnel will determine the latitude and longitude. The latitude and longitude will be entered into a geographic information system (GIS). To confirm latitude and longitude locations (if provided) or to determine the location of the source, a follow-up telephone call will be made during which the CWS contact will verbally describe the location of the well or intake to USGS personnel. USGS personnel then will locate the source, using Delorme Street Atlas/TopoUSA (Delorme, Yarmouth, Maine), and determine the latitude and longitude. The CWSs also will be asked to verbally provide information missing on the written questionnaire, if the information is available to them. This ancillary information will be used to identify important natural and anthropogenic factors that may relate to the occurrence and concentration of MTBE and other VOCs observed in the source water.

Focused Source-Water Survey

The Focused Source-Water Survey will determine the frequency of detection, the range in concentrations, and the temporal variation of MTBE, three other ether gasoline oxygenates, and 62 other VOCs (table 1) in drinking-water sources. In addition, the

occurrence and range in concentrations of ether oxygenate degradation products will be determined. The design of the Focused Survey will be based partly on factors that are suspected or known to be related to frequent detection of MTBE and other VOCs in source water. The survey will be conducted in two parts: (1) CWSs with source water suspected of having concentrations of MTBE, and (2) CWSs with source waters with known concentrations of MTBE. This design will allow sampling to begin in areas where MTBE is suspected to occur and also will allow the flexibility to redirect sampling as new water-quality data become available from, for example, the Random Source-Water Survey.

The distribution of samples for the Focused Source-Water Survey by type of drinking-water source and sample frequency is shown in table 7. About 480 samples will be collected from CWSs and distributed among drinking-water sources. Eighty wells sampled biannually, 40 reservoirs and lakes sampled quarterly, and 20 rivers and streams sampled eight times per year will be used in the Focused Source-Water Survey. Samples will be collected multiple times from each source water in the Focused Source-Water Survey to evaluate temporal variations on MTBE and other VOC concentrations. For example, variations in MTBE and VOC concentrations are thought to be most evident for surface-water samples collected during spring and summer months (frequent watercraft use) than in those samples collected during the fall and winter months when watercraft use is infrequent. All drinking-water sources vulnerable to MTBE and other VOCs that are utilized by the CWSs will be considered as candidates for the survey. Therefore, it will be possible for one CWS to have samples collected from all three source-water categories listed in table 7.

Table 7. Number of source-water types and sampling frequency for the Focused Source-Water Survey

Source water	Number of sources	Sampling frequency	Total number of samples
Ground water	80	Biannually	160
Reservoirs and lakes	40	Quarterly	160
Rivers and streams	20	Eight per year	160
Total	140		480

As part of the design of the Focused Source-Water Survey, control source-water sites for MTBE will be selected. The control source water sites will be included in the total number of sources in table 7. These will be source water in areas where there is no known use of MTBE in gasoline. Two wells, one river, and one reservoir will be selected for control sites. The wells will be located in selected urban areas and will withdraw their water from unconfined, unconsolidated aquifer materials. The river and reservoir sources selected will have frequent watercraft use.

Community Water Supplies with Suspected Methyl *tert*-Butyl Ether Contamination

CWS source water located in hydrologic, climatic, and demographic settings that are suspected of being especially vulnerable to MTBE contamination will be selected initially. CWS sources that meet the following criteria will be selected for sampling: (1) highly urbanized, high population-density settings, in areas where reformulated and oxygenated gasoline is required, especially in areas of high precipitation and high recharge rates where VOCs may be transported quickly to shallow ground water, and (2) reservoirs, lakes, and large rivers that are used by watercraft, especially in areas where MTBE is in use.

CWS sources suspected of being contaminated with MTBE initially will be selected in metropolitan areas with populations greater than 250,000 and where gasoline used in the area contains MTBE. Much of the MTBE use in the United States occurs in RFG designated areas, and about 80 percent of RFG contains MTBE to achieve a specified minimum oxygen content. Recent findings for shallow ground water (less than 200-foot well depth) indicate that the use of MTBE in gasoline in RFG and OXY areas increases the probability of detecting MTBE in ground water by as much as a factor of six (P.J. Squillace, U.S. Geological Survey, written commun., 1999). It is estimated that approximately 20 million of the 50 million people who use drinking-water supplies from ground water in RFG and OXY areas use a water supply that is considered vulnerable to contamination by MTBE, other ether gasoline oxygenates, and other VOCs (P.J. Squillace, U.S. Geological Survey, written commun., 1999). The vulnerability of aquifers to MTBE contamination appears to be related mostly to use of MTBE in gasoline, the density of above-ground and underground storage tanks, and soil erodibility (Squillace and Moran, 2000). Other factors, such as

well depth and depth to ground-water, and the presence of roads seem to be less important.

A total of 139 of the largest cities and metropolitan areas in the United States were identified by USGS from 1992 census data projections. Of the 139 largest cities and metropolitan areas, 27 were determined to be in RFG areas or in the “opted-in” RFG program (U.S. Environmental Protection Agency, 1999a). Thirteen of the 139 cities and metropolitan areas were determined to be in OXY gasoline areas where ethanol is the primary oxygenate in gasoline (U.S. Environmental Protection Agency, 1999b).

The Motor Gas Survey, which provides chemical analyses of gasoline collected from 111 select metropolitan locations across the United States, has included ether oxygenate analyses by an independent firm (TWR Systems and Information Technology Group, Bartlesville, Oklahoma) since about 1991. The most recent data from this survey, collected from 1996 and 1997, were used to compare MTBE concentrations in gasoline in the 139 large cities and metropolitan areas. Where MTBE was detected in gasoline, the concentrations were either less than 1 percent by volume, or approximately 10 percent by volume. Metropolitan areas using RFG gasoline were found to have the highest MTBE concentrations in gasoline. Lower concentrations of MTBE likely are due to its use as an octane enhancer.

On the basis of population density, federally designated RFG/OXY areas, and MTBE data from gasoline analyses, 14 metropolitan areas will be selected initially for the Focused Source-Water Survey. All selected metropolitan areas will have populations greater than 250,000, with MTBE concentrations in gasoline equal to or greater than 10 percent by volume as determined from the Motor Gas Survey (table 8). When considering the CWSs that serve more than 50,000 people, about 2.6 percent of all CWSs located in the 14 metropolitan areas fall into the very large source-size category. These CWSs provide water to more than 75 percent of the population served within those 14 metropolitan areas. These will be the CWSs chosen initially. CWSs that purchase water from a wholesaler will not be considered for this survey. Table 9 lists the type of sources to be sampled in each metropolitan area. The number of sampling sites will be distributed among the 14 metropolitan areas on the basis of population. Therefore, of the 14 metropolitan areas, the more populated areas will have more sampling sites in comparison to less populated areas.

Table 8. Metropolitan areas where methyl *tert*-butyl ether is used extensively in gasoline

[MSA, Metropolitan Statistical Area; NECMA, New England County Metropolitan Area; CMSA, Consolidated Metropolitan Statistical Area]

Identifier	Metropolitan area
1	Bakersfield, CA (MSA)
2	Boston, MA (NECMA)
3	Dallas-Ft. Worth, TX (CMSA)
4	Hartford, CT (NECMA)
5	Houston-Galveston-Brazoria, TX (CMSA)
6	Los Angeles-Riverside-Orange County, CA (CMSA)
7	Louisville, KY-IN (MSA)
8	New York-Northern New Jersey-Long Island, NY-NJ (CMSA)
9	Philadelphia-Wilmington-Atlantic City, PA-NJ-DE-MD (CMSA)
10	Providence-Fall River-Warwick, RI-MA (NECMA)
11	Richmond-Petersburg, VA (MSA)
12	San Diego, CA (MSA)
13	San Francisco-Oakland-San Jose, CA (CMSA)
14	Washington-Baltimore, DC-MD-VA-WV (CMSA)

Table 9. Number of community water sources to be sampled in 14 metropolitan areas suspected to have concentrations of methyl *tert*-butyl ether in source waters

Identifier	Metropolitan area (table 8)	Number of ground-water sources	Number of river/stream sources	Number of reservoir/lake sources
1	Bakersfield	2	1	1
2	Boston	2	1	1
3	Dallas	2	1	1
4	Hartford	2	1	1
5	Houston	2	1	1
6	Los Angeles	4	1	2
7	Louisville	2	1	1
8	New York	4	1	2
9	Philadelphia	4	1	2
10	Providence	2	1	1
11	Richmond	2	1	1
12	San Diego	2	1	1
13	San Francisco	4	1	2
14	Washington, D.C.	4	1	2
Totals		38	14	19

Some States do not have RFG or OXY gasoline program areas; however, these States may have areas that have a high detection frequency of MTBE in ground water at LUST and gasoline spill sites. Discussions with underground-storage-tank and drinking-water officials, water suppliers, and USGS personnel will help gain a better understanding of MTBE releases to source water in these States. Additional candidate aquifers, streams, and rivers for the Focused Source-Water Survey are expected to be identified through

these discussions. Some reservoirs and lakes that have frequent recreational use in former RFG areas or near (within 100 miles) current RFG areas are suspected of having detectable MTBE concentrations. The number and national distribution of these sources are listed in table 10 by State and source-size categories. The source-size categories are identical to those used in the Random Source-Water Survey (for example, the very large category is greater than 50,000 served).

Table 10. Number of community drinking-water sources suspected of having concentrations of methyl *tert*-butyl ether by State and source-size category

[GW, ground water; SW, surface water; VSM, very small; SM, small; MED, medium; LRG, large; VLRG, very large]

State ¹	Source-size category										Total
	GW-VSM	GW-SM	GW-MED	GW-LRG	GW-VLRG	SW-VSM	SW-SM	SW-MED	SW-LRG	SW-VLRG	
CA	0	0	2	4	7	0	0	0	1	6	20
CO	0	0	0	0	0	0	0	0	0	1	1
CT	0	0	0	2	1	0	1	0	0	0	4
DE	2	2	3	0	1	0	0	0	0	2	10
GA	0	0	0	1	0	0	0	0	0	2	3
IN	0	0	0	0	0	0	0	0	0	1	1
KY	0	0	0	2	0	0	0	0	0	1	3
LA	0	0	0	0	0	0	0	0	0	1	1
MA	0	0	0	0	0	0	0	0	0	2	2
MD	0	0	0	0	0	0	0	0	0	1	1
MS	0	0	0	0	0	0	0	0	0	1	1
NJ	0	0	0	0	0	0	0	0	0	1	1
NV	0	0	0	0	0	0	0	0	0	1	1
NY	0	0	0	0	4	0	0	0	0	0	4
OK	0	0	0	0	0	0	0	0	0	2	2
OR	0	0	1	3	0	0	1	1	0	0	6
PA	0	0	0	0	0	0	0	0	0	3	3
RI	0	0	0	0	0	0	0	0	0	1	1
TX	0	1	0	0	2	0	0	0	0	3	6
VA	0	0	0	0	0	0	0	0	0	3	3
VT	0	0	0	0	0	0	0	0	0	1	1
WV	0	0	2	0	0	0	0	0	0	0	2
Total	2	3	8	12	14	0	2	1	1	33	77

¹Postal Service State abbreviation.

Community Water Systems with Known Methyl *tert*-Butyl Ether Contamination

This part of the Focused Survey concerns water sources with known MTBE occurrences. CWSs will be selected on the basis of the following criteria:

(1) MTBE is known to occur in the source water on the basis of recently completed or ongoing sampling activities, and (2) verbal communication from local, State, or other Federal agency personnel indicates the presence of MTBE in the source water. Source-water samples analyzed from the Random Source-Water Survey that are determined to contain concentrations of MTBE greater than or equal to 0.5 µg/L will be

included in the Focused Source-Water Survey to expand the amount of data pertaining to contaminated source water. In addition, information gained from a 12-State drinking-water retrospective (Grady and Casey, 2001), recent reports completed by the States of Maine and California (Keller and others, 1998), and other ancillary information (State data bases, university studies, and media accounts of MTBE spills) as it becomes available will be used to select CWSs to be included in the Focused Source-Water Survey. Table 11 provides a summary of the states and source-size categories of CWSs with sources having known occurrences of MTBE.

Table 11. Number of community drinking-water sources with known concentrations of methyl *tert*-butyl ether by State and source-size category

[GW, ground water; SW, surface water; VSM, very small; SM, small; MED, medium; LRG, large; VLRG, very large]

State ¹	Source-size category										Total
	GW-VSM	GW-SM	GW-MED	GW-LRG	GW-VLRG	SW-VSM	SW-SM	SW-MED	SW-LRG	SW-VLRG	
AZ	0	0	0	1	0	0	0	0	0	1	2
CA	0	0	0	0	0	0	1	0	0	8	9
CT	0	1	0	0	0	0	0	0	0	0	1
DE	0	0	0	1	0	0	0	0	0	0	1
FL	0	0	0	0	2	0	0	0	0	1	3
IA	1	1	0	0	0	0	0	0	0	0	2
IL	0	2	2	0	0	0	0	0	0	0	4
KY	1	0	0	0	0	0	0	0	0	0	1
KS	0	2	1	1	0	0	0	0	0	0	4
MA	1	0	0	1	0	0	0	0	0	0	2
MD	0	1	1	1	0	0	0	0	0	0	3
ME	0	1	2	1	0	0	0	0	0	0	4
NC	0	0	1	0	0	0	0	0	0	1	2
NH	0	0	1	1	0	0	0	0	1	1	4
NJ	0	0	0	1	3	0	0	0	0	0	4
NY	0	0	0	0	1	0	0	0	0	0	1
OH	0	1	0	0	0	0	0	0	0	0	1
OR	2	0	0	0	0	0	0	0	0	0	2
PA	1	0	0	0	0	0	0	0	0	1	2
TN	0	0	0	0	0	0	0	0	1	0	1
TX	0	0	0	0	0	0	1	0	0	2	3
VA	0	1	0	0	0	0	0	0	0	0	1
Total	6	10	8	8	6	0	2	0	2	15	57

¹Postal Service State abbreviation.

Ancillary Information Collection

As with the Random Source-Water Survey, ancillary information on each CWS and source water will be collected for the Focused Source-Water Survey. The information will be used for spatial and temporal analysis and to determine possible relations between the occurrence of MTBE in the source-water samples and anthropogenic factors. Similar ancillary information for the Focused Source-Water Survey as for the Random Source-Water Survey is sought: latitude/longitude of the sources sampled, population served, source characteristics, MTBE and other gasoline oxygenate use data and designated program areas, and known or potential VOC point-source locations.

A short telephone questionnaire will be completed during the initial interview with the participating CWS staff to identify the contact person and get additional information on the source water. A written, more detailed questionnaire (Appendix B) will be delivered to the CWS contact by the USGS sampling personnel. The written questionnaire for the Focused Source-Water Survey requests similar information (intake/well location, water treatment, any known or potential VOC point-source locations, well characteristics, watershed protection) as the written questionnaire for the Random Source-Water Survey. The USGS sampling personnel will provide the location (latitude/longitude) of the source water either in the form of a point on a topographic map or global positioning system (GPS) coordinates.

SUMMARY

A national survey design will provide information on the frequency of detection, concentration, distribution, and temporal variability of methyl *tert*-butyl ether (MTBE), other ether gasoline oxygenates, and other volatile organic compounds (VOCs) in source water used by community water systems (CWSs) in the United States. The national survey will be conducted by the U.S. Geological Survey (USGS) in collaboration with Metropolitan Water District of Southern California (MWDSC) and the Oregon Graduate Institute of Science and Technology (OGI). The survey is sponsored by the American Water Works Association Research Foundation.

The national survey will be accomplished in two stages. The first stage, the Random Source-Water

Survey, will provide an unbiased sample of source water for 1,000 CWSs that will represent the more than 54,000 CWSs in the 50 States, Native American Lands, and Puerto Rico. One sample will be collected for each CWS. The allocation of CWSs in the Random Source-Water Survey is stratified by several factors—the total number of systems within each of the five population served-size categories, source of water (ground or surface water), and the total number of people served by each of the source-size category. There will be a total of 10 categories in the Random Source-Water Survey. The 1,000 source-water samples will be collected from 613 ground-water-supplied CWSs (wells, springs, and galleries) and 387 supplied by surface water (rivers, aqueducts, canals, lakes, and reservoirs). Source-water samples and field blanks will be collected by CWS personnel.

The design of the second stage of the national survey, the Focused Source-Water Survey, is based on factors that appear or are known to be related to frequent detection of MTBE and other VOCs. These factors include ground- and surface-water sources in highly urbanized areas where reformulated and oxygenated gasolines are used, reservoirs and rivers used by watercraft in areas where MTBE is in use, and any drinking-water sources known to contain MTBE and other VOCs from previous investigations. About 480 samples will be collected from 140 CWSs categorized by three drinking-water-source types. Eighty wells sampled biannually, 40 reservoirs and lakes sampled quarterly, and 20 rivers and streams sampled eight times per year will be included. Environmental and quality-control/quality-assurance samples for the Focused Source-Water Survey will be collected by USGS personnel using USGS ground- and surface-water protocols.

Samples for both the Random and Focused Source-Water Surveys will be analyzed for MTBE, three other ether gasoline oxygenates, and 62 other VOCs by MWDSC using U.S. Environmental Protection Agency method 524.2. Duplicate samples will be collected with about one-half of the Focused Source-Water samples and analyzed for oxygenate degradation products using a sensitive detection method developed by the OGI. Ancillary information, such as latitude and longitude, source characteristics, and any known or potential VOC point source, will be obtained from participating CWSs for both the Random and Focused Source-Water Surveys using telephone interviews with

CWS personnel and written questionnaires. This information will be used to further explain anthropogenic factors and the frequency and concentration of MTBE and other VOCs in source water.

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APPENDICES

Appendix A

AWWARF MTBE NATIONAL STUDY OF MTBE AND OTHER VOCs RANDOM SURVEY MAIL-IN QUESTIONNAIRE

Please complete the following questionnaire and return it with the sample kit.

GENERAL INFORMATION

1. Water System Name
2. PWSID #
3. Contact
 - Name _____ Title _____
 - Signature _____
 - Street _____ Phone _____ ext _____
 - City _____ FAX _____
 - State _____ Zip _____ email _____
4. Source water chosen for this study?
 - a) Groundwater
 - b) Surface Water
5. How often do you monitor volatile organic compounds (VOCs) in the source being monitored in this study?
 - quarterly
 - monthly
 - other
6. Do you monitor?
 - source water
 - finished water
 - both
7. Has MTBE been detected in *this* source within the last 3 years?
 - a) In the source water? Yes ___ No ___ Uncertain ___
 - b) In the finished water? Yes ___ No ___ Uncertain ___
8. Have other VOCs (excluding trihalomethanes and other disinfection by-products) been detected in this source within the last 3 years?
 - a) In the source water? Yes ___ No ___ Uncertain ___
 - b) In the finished water? Yes ___ No ___ Uncertain ___

9. Fuel information

a) Is the source water in an ozone non-attainment area?

Yes ____ No ____ Uncertain ____

b) Is reformulated gasoline required in the area of the source water?

Yes ____ No ____ Uncertain ____

GROUNDWATER

IF SOURCE IS SURFACE WATER, SKIP TO PAGE 5

ANSWER FOLLOWING QUESTIONS FOR THE GROUNDWATER SOURCE BEING SAMPLED FOR THIS STUDY:

1. Source name

2. Source type

well

spring

gallery

3. Location of source

a) latitude _____ and longitude _____ unknown _____

1) From GPS? Yes ___ No___

2) From map? Yes ___ No___

3) From other?

b) Please send a map showing location of the well (USGS 1=24000 topographic preferable), if available.

a) What is the precise (i.e., 911 emergency location) address for the source location, if known?

Street

City

State

zip code

4. If source is a well please indicate depth

a) Of the well (from land surface) ft.

b) Of the pump intake ft.

c) to the water level

1) Static ft.

2) Pumping ft.

5. Well yield:

a) Average volume pumped per day gallons

b) Number of days well is used

1) per month ***or***

2) per year

6. Well construction

a) Type of finish

- 1) screened
- 2) open hole
- 3) uncertain

b) Length of screened or open interval

7. Aquifer information

a) lithology (composition)

- 1) consolidated (bedrock) Yes ___ No___ Uncertain ___
- 2) unconsolidated (sand or gravel) Yes ___ No___ Uncertain ___

b) aquifer condition

- 1) Confined (artesian) Yes ___ No___ Uncertain ___
- 2) Unconfined (water table) Yes ___ No___ Uncertain ___

c) surface water influence

- 1) Is this source perceived or known to be “under the influence” of surface water?
Yes___ No___ Uncertain___

- 2) How far away is the nearest surface-water body?

d) protection

- 1) Are there any petroleum refineries, pipelines, gas stations, or chemical underground storage tanks within ¼ mile of the sampled source?

Yes___ No___ Uncertain

- 2) Are there any known contaminant sources in proximity to the sampled source (e.g., gas stations within ¼ mile, fuels or chemicals stored in well pump house, gasoline generator in the immediate vicinity of the pump, or other sources of VOCs) that may impact the sampled source?

Yes___ No___ Uncertain

- 1) Are there any natural oil fields present near (within a ¼ mile) the area of sampled source?

Yes___ No___ Uncertain

- 2) Has this well or any wells within the same wellfield (within approximately ¼ mile) been closed (within the last 3 years) due to contamination from VOCs.

Yes___ No___ Uncertain

8. Has there been any unusual storm events in the past two months.

Yes___ No___ If yes, describe:

SURFACE WATER

IF SOURCE IS GROUND WATER, SKIP TO PAGE 8

ANSWER FOLLOWING QUESTIONS FOR THE SOURCE BEING SAMPLED FOR THE STUDY:

1. Source name
2. Source type
 - a) reservoir
 - b) lake
 - c) river
 - d) other
3. Watershed information (of source sampled in this project)
 - a) Is there a pollution prevention program?
Yes ____ No ____
Please ***briefly*** describe:

 - b) Are there any known contaminant sources in proximity to the **intake** of this water source (e.g., gas stations within ¼ mile, chlorinated solvent storage or known point source discharges to streams)?
Yes ____ No ____ Uncertain____
 - c) Are there any petroleum refineries, fuel pipelines, gasoline stations or chemical storage tanks within ¼ mile of the **intake** of this surface water source?
 - 1) Yes ____ No ____ Uncertain____
 - 2) Please describe:

d) Are there any natural oil fields present within a ¼ mile of the **intake** of this area?

1) Yes ___ No ___ Uncertain___

2) Please describe:

e) Is any fuel or chemical that might be a source of VOCs commercially transported on the source (i.e., river) and within ¼ mile of the **intake**?

Yes ___ No ___ Uncertain___

4. Multi-use sources

a) Are private motorized water craft operated on the water source?

Yes ___ No ___

b) Are official use motorized water craft operated on the water source?

Yes ___ No ___

c) Estimate of types of vehicles on the water source

	0-10	10-50	>100	Daily/monthly
two stroke engine boats				
four stroke engine boats				
personal watercraft (i.e., jetskis)				

d) Are there any motor craft restrictions?

1) Horsepower restrictions? Yes ___ No ___

2) Boat number restrictions Yes ___ No ___

3) Other

5. Intake (principal source) information

a) distance from shoreline to intake opening

b) depth (below mean water level) of intake

- c) intake diameter
- d) intake construction material
- e) pumped or gravity flow
- f) distance to sample port
- g) latitude _____ and longitude _____ unknown _____

1) From GPS? Yes ___ No___

2) From map? Yes ___ No___

3) From other?

h) Is there a tiered tower at the intake to allow for selective depth withdrawal from the lake?

1) Yes ___ No ___

2) At what depths can water be withdrawn

meters, feet

meters, feet

meters, feet

meters, feet

meters, feet

meters, feet

meters, feet

meters, feet

6. Size information

a) Surface area of lake or reservoir

b) Average depth of the lake/reservoir

c) Storage volume of lake or reservoir

d) River/stream flow _____ MGD

CFS

e) Does the lake/reservoir stratify during the year?

1) Yes ___ No ___ Uncertain

2) During what months

f) Does the source freeze over in the winter? Yes ___ No ___

7. Please send a map showing location of the intake (USGS 1=24000 topographic preferable), if available.

8. Has there been any unusual storm events in the past two months.

Yes ___ No ___ If yes, describe:

TREATMENT

ANSWER FOLLOWING IF TREATMENT OF SOURCE SAMPLED IS TREATED PRIOR TO SERVING

1. Treatment plant name
2. What treatments are used on the source water prior to final distribution?
 - a) Groundwater treatment
 - 1) disinfection Yes ___ No ___
 - 2) aeration Yes ___ No ___
 - 3) iron/manganese removal Yes ___ No ___
 - 4) oxidation Yes ___ No ___
 - 5) other Yes ___ No ___
 - b) Surface water treatment
 - 1) disinfection Yes ___ No ___
 - 2) conventional filtration Yes ___ No ___
 - 3) direct filtration Yes ___ No ___
 - 4) in-line filtration Yes ___ No ___
 - 5) slow sand filtration Yes ___ No ___
 - 6) softening Yes ___ No ___
 - 7) two-stage softening Yes ___ No ___
 - 8) coagulation/sedimentation/softening Yes ___ No ___
 - 9) split treatment/softening Yes ___ No ___
 - 10) complex parallel train softening Yes ___ No ___
 - 11) membrane treatment Yes ___ No ___
 - 12) powder activated carbon Yes ___ No ___
 - 13) no treatment (filtration avoidance) Yes ___ No ___
 - 14) other Yes ___ No ___
 - c) Is treatment designed to remove volatile or synthetic organics compounds?
 - 1) granular activated carbon
 - 2) powdered activated carbon
 - 3) membrane
 - 4) ozone
 - 5) aeration
 - 6) air stripping towers
 - 7) other (please describe)
3. Please send a flow diagram of the system, if available?
4. Plant output capacity (MGD)

Appendix B

AWWARF MTBE NATIONAL STUDY OF MTBE AND OTHER VOCs

FOCUSED SURVEY

MAIL-IN QUESTIONNAIRE

Please complete the following questionnaire and return in the enclosed envelope. Your participation in this study is greatly appreciated

GENERAL INFORMATION

1. Water System Name

2. PWSID #

3. Contact

Name

Title

Signature _____

Street

Phone

ext

City

FAX

State

Zip

email

4. Source waters (check)?

Groundwater

Surface Water

5. How often do you monitor volatile organic compounds (VOCs)?

Groundwater

Surface Water

quarterly

monthly

other

6. Do you monitor for VOCs?

raw water (prior to treatment)

finished water

both

7. Has MTBE been detected in **any** source within the last 3 years?

a) Yes ____ No ____

b) Name of sources where MTBE has been detected

8. Have other VOCs (excluding trihalomethanes and other disinfection by-products) been detected in this source within the last 3 years?

a) Yes ____ No ____

b) Name of sources where other VOCs have been detected

9. Fuel information

a) Are any of the source waters in an ozone non-attainment area?

Yes ____ No ____ Uncertain ____

b) Name of sources in ozone non-attainment areas

c) Is reformulated gasoline required in the area of the source water?

Yes ____ No ____ Uncertain ____

10. Watershed information (of sources sampled in this project)

Is there a pollution prevention program? Yes ____ No ____

Please *briefly* describe:

11. Please send maps (if available) showing location of the aquifers, wells, and surface water locations (USGS 1=24000 topographic preferable), that are being sampled in this project.

12. Has there been any unusual storm events within the last two months.

Yes____ No____ If yes, describe:

13. Please complete:

a) Table D.1 and D,2 for groundwater sources to be sampled

b) Table D.3 through D.5 for surface water sources to be sampled.

c) Table D.6 for treatment plant information

Table D.1

Aquifer Information

Aquifer Name	Type			Number of wells, springs, galleries in aquifer	Name of well (spring or gallery) sampled in this project	Aquifer Lithology		Aquifer Condition		Under influence of surface water (Yes/No)
	Well	Spring	Gallery			Consolidate (bedrock)	unconsolidated (sand or gravel)	confined (artesian)	Unconfined (water table)	

Table D.2

Well (Spring or Gallery) Information (for wells, springs, or galleries sampled)

Well (Spring or Gallery) Name	Latitude and longitude*	Depth from land surface	Depth of pump intake	Depth to water level (ft)	Pump-ing	Finish	Length of screened interval	Volume pumped	Average Number days
				Static		Screen-ed		Gallons/day	Per month

* Is Latitude/longitude from:

GPS? Yes ___ No ___

Map? Yes ___ No ___

From other? _____

Table D.3

Surface Source Water Information

Source	Type (reservoir, lake, river, or stream)	Surface area of lake/reser- voir (acre-ft)	Average depth (ft)	Storage volume of lake or reservoir (ft ³)	Does lake/reser- voir stratify (Yes/No)	Months lake/reser- voir stratifies	Does source freeze over in winter (Yes/No)	River /stream flow (cfs)

Acre-ft- acre feet

Ft. - feet

Cfs - cubic feet per second

Table D.4

Surface Water Intake Information

Source	Latitude & longitude*	Tiered outlet tower (yes/no)	Depth of tiered intakes (ft)	Intake			
				Distance from shoreline	Depth (minimum) below water level	Diameter	Pumped or gravity feed

* Is Latitude/longitude from:

GPS? Yes ___ No ___

Map? Yes ___ No ___

From other? _____

Table D.5

Multi-use Source Information

Source Name	Motorized Water Craft (check those that apply)		Type of Vehicles (check those that apply)				Restrictions (check those that apply)	
	Private use	Official Use only	Two Stroke engines (#/month)	Four Stroke engines (#/month)	Personal Water Craft (e.g., jetskis) (#/month)	Horsepower restrictions	Maximum number of boats allowed	

Other restrictions (please describe):

Table D.6

Treatment Plant Information

Treatment Plant Name:				
Source Water treated:				
Plant capacity (mgd)				
Type of Treatment				
Groundwater Treatment				
	Disinfection			
	Aeration			
	Iron/manganese removal			
	Oxidation			
	Other			
Surface Water treatment				
	Disinfection			
	Conventional filtration			
	Direct filtration			
	In-line filtration			
	Slow sand filtration			
	Softening			
	Two-stage softening			
	Coag/sed/softening			
	Split treatment/softening			
	Parallel train softening			
	Membrane treatment			
	PAC			
	None*			
	Other			
	Treatment for VOC removal			

Coag/sed/softening - coagulation, sedimentation and softening
PAC - Powder activated carbon

*** filtration avoidance**