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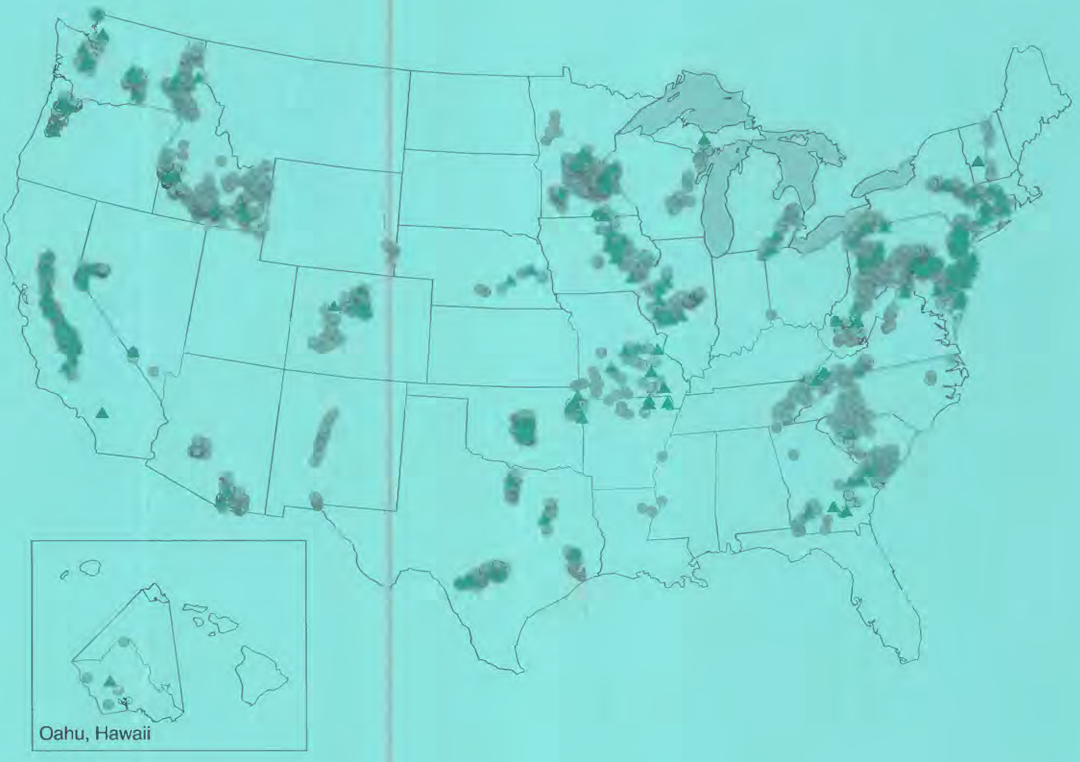
NATIONAL SYNTHESIS ON VOLATILE ORGANIC COMPOUNDS

Occurrence and Status of Volatile Organic Compounds in Ground Water from Rural, Untreated, Self-Supplied Domestic Wells in the United States, 1986-99

Water-Resources Investigations Report 02-4085



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Water Resources Division
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MEMORANDUM

September 10, 2002

To: Distribution List for Publications on Volatile Organic Compounds (VOCs)

From: John S. Zogorski, JSZ Project Chief, VOC National Synthesis,
National Water-Quality Assessment (NAWQA) Program

Subject: USGS publication on VOCs in domestic wells

Enclosed is a recent publication by U.S. Geological Survey authors. Please circulate the information in this mailing to others in your office who have an interest in volatile organic compounds (VOCs). Additional complementary copies of the enclosed report can be obtained by contacting Erika Schoen at the address listed above, or telephone ext. 265, or email eschoen@usgs.gov. Should you wish to be removed from this distribution list, please contact Erika Schoen. If you would prefer to periodically receive notice of new publications via email, please send an email to eschoen@usgs.gov with 'pub distribution' in the subject line.

The Water Resources Investigations Report by Mike Moran, Wayne Lapham, Barbara Rowe and John Zogorski titled "Occurrence and Status of Volatile Organic Compounds in Ground Water from Rural, Untreated, Self-Supplied Domestic Wells in the United States, 1986-99," characterizes the occurrence and status of VOCs in domestic well water samples collected as part of the NAWQA program, as well as existing sample data from local, State, and other Federal agencies. Major topics related to the occurrence and status of VOCs in these samples include detections of individual as well as mixtures of VOCs, detections of VOCs by predominant use group, and status of VOC concentrations compared to federal maximum contaminant levels and health advisories. Potential sources of VOCs are also discussed. Inquiries and technical questions about the report can be addressed to Mike Moran at (605) 355-4560 ext. 244, or email mjmoran@usgs.gov.

This publication is also available in pdf format on the NAWQA VOC National Synthesis home page at http://water.usgs.gov/nawqa/vocs.

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

Occurrence and Status of Volatile Organic Compounds in Ground Water from Rural, Untreated, Self-Supplied Domestic Wells in the United States, 1986-99

By Michael J. Moran, Wayne W. Lapham, Barbara L. Rowe, and John S. Zogorski

Water-Resources Investigations Report 02-4085

U.S. Department of the Interior

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Rapid City, South Dakota: 2002

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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 suifor 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

Robert M. Hirsch
Associate Director for Water

CONTENTS

FIGURES

FIGURES—Continued

TABLES

CONVERSION FACTORS, ABBREVIATIONS, AND ACRONYMS

Multiply	By	To obtain
acre	4,047	square meter
acre	0.4047	hectare
square mile (mi^2)	259.0	hectare
square mile (mi^2)	2.590	square kilometer
gallons (gal)	3.785	liters
gallon per day (gal/d)	0.003785	cubic meter per day
million gallons per day (Mgal/d)	0.04381	cubic meter per second
ounce (oz)	28.35	grams

μg/L	micrograms per liter
km^2	square kilometers
mL	milliliter
g/cm^3	gram per cubic centimeter
AST	Aboveground Storage Tank
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes
CAA	Clean Air Act
CWS	Community Water System
DWA	Drinking Water Advisory
GC/MS	Gas Chromatography/Mass Spectrometry
GWSI	U.S. Geological Survey Ground-Water Site Inventory
HA	Health Advisory
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
NAAQS	National Ambient Air Quality Standards
NAWQA	U.S. Geological Survey National Water-Quality Assessment Program
NTNCWS	Non-Transient Non-Community Water System
NWIS	U.S. Geological Survey National Water Information System
NWQL	U.S. Geological Survey National Water-Quality Laboratory
OXY	Oxygenated Gasoline
QA	Quality Assurance
QC	Quality Control
PWS	Public Water System
RFG	Reformulated Gasoline
SDWA	Safe Drinking Water Act
THMs	Trihalomethanes (bromodichloromethane, chlorodibromomethane, tribromomethane, trichloromethane)
TRI	U.S. Environmental Protection Agency Toxics Release Inventory
USGS	U.S. Geological Survey
USEPA	U.S. Environmental Protection Agency
UST	Underground Storage Tank
VOCs	Volatile Organic Compounds

COMMON SYNONYMS AND ABBREVIATIONS OF SELECTED VOLATILE ORGANIC COMPOUNDS

IUPAC Name	**Common Synonym or Abbreviation**
(1-Methylethyl)benzene	Isopropylbenzene
1,1,1-Trichloroethane	Methyl chloroform
1,1,2-Trichloro-1,2,2-trifluoroethane	Freon 113, CFC 113
1,1-Dichloroethane	Ethylidene dichloride
1,2-Dibromo-3-chloropropane	DBCP
1,2-Dibromoethane	EDB
1,2-Dichlorobenzene	*o*-Dichlorobenzene
1,2-Dichloroethane	Ethylene dichloride
1,2-Dimethylbenzene	*o*-Xylene
1,3-Dichlorobenzene	*m*-Dichlorobenzene
1,3-Dimethylbenzene	*m*-Xylene
1,4-Dichlorobenzene	*p*-Dichlorobenzene
1,4-Dimethylbenzene	*p*-Xylene
2-Propenal	Acrolein
2-Propenitrile	Acrylonitrile
Bromoethene	Vinyl bromide
Bromomethane	Methyl bromide
Chloroethane	Ethyl chloride
Chloroethene	Vinyl chloride
Chloromethane	Methyl chloride
Dichlorodifluoromethane	Freon 12, CFC 12
Dichloromethane	Methylene chloride
Diisopropyl ether	DIPE
Ethenylbenzene	Styrene
Ethyl *tert*-butyl ether	ETBE
Methyl *tert*-butyl ether	MTBE
Methylbenzene	Toluene
tert-Amyl methyl ether	TAME
Tetrachloroethene	PCE
Tetrachloromethane	Carbon tetrachloride
Tribromomethane	Bromoform
Trichloroethene	TCE
Trichlorofluoromethane	Freon 11, CFC 11
Trichloromethane	Chloroform

DEFINITIONS OF SELECTED TERMS USED IN THIS REPORT

Term	**Definition**
Assessment level	A level of censoring applied to water-quality data that have variable laboratory reporting levels either between subsets of VOC analytes or between individual VOC analytes. The assessment level is applied to data received from the laboratory and is applied subsequent to the laboratory reporting level. The primary purpose of the assessment level is for accurate comparison of detection frequencies between subsets of VOC analytes or between individual VOC analytes.
Domestic well	A self-supplied ground-water source for household water.
Domestic well water	Untreated ground water collected from rural, self-supplied domestic wells at the wellhead.
Drinking-water criteria	Drinking-water-quality measure that is not enforceable.
Drinking-water standard	Drinking-water-quality measure that is enforceable.
Finished drinking water	Water after treatment that might have been blended from multiple untreated water sources.
Laboratory reporting level	A level of reporting concentrations of VOCs that is set by the laboratory to minimize the rate of false positives and false negatives. Concentration below the laboratory reporting level are denoted by a "<" preceding a concentration value.
Occurrence	The presence or absence, frequencies of detection, concentrations, and ranges of concentrations of VOCs and the locations (areal patterns) of VOC detections in ground water.
Rural areas	Areas that have a population density of less than 386 persons/km^2 (1,000 persons/mi^2 or 1.56 persons/acre).
Self-supplied water	Water withdrawn from a source by a user rather than being obtained from a public supply.
Status	Comparison of VOC concentrations relative to drinking-water standards, criteria, and taste and odor thresholds.
Target analyte	One of 55 volatile organic compounds given emphasis in the U.S. Geological Survey's National Water-Quality Assessment Program.
VOCs by group	VOCs grouped by the primary use of each VOC.

Occurrence and Status of Volatile Organic Compounds in Ground Water from Rural, Untreated, Self-Supplied Domestic Wells in the United States, 1986-99

By Michael J. Moran, Wayne W. Lapham, Barbara L. Rowe, *and* John S. Zogorski

ABSTRACT

Samples of untreated ground water from 1,926 rural, self-supplied domestic wells were analyzed for volatile organic compounds (VOCs) during 1986-99. This information was used to characterize the occurrence and status of VOCs in domestic well water. The samples were either collected as part of the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program occurrence-assessment studies or were compiled by NAWQA from existing ambient ground-water or source-water-quality monitoring programs conducted by local, State, and other Federal agencies. Water samples were collected at the wellhead prior to treatment or storage. In most samples, 55 target VOCs were analyzed, and occurrence and status information generally was computed at an assessment level of 0.2 μg/L (microgram per liter).

At least one VOC was detected in 12 percent of samples (232 samples) at an assessment level of 0.2 μg/L. This detection frequency is relatively low compared to the 26 percent detection frequency of at least one VOC in public supply wells sampled by NAWQA, and the difference may be due, in part, to the higher pumping rates, pumping stress factors, and larger contributing areas of public supply wells. Samples with detections of at least one VOC were collected from wells located in 31 of 39 States.

Solvents were the most frequently detected VOC group with detections in 4.6 percent of samples (89 samples) at an assessment level of 0.2 μg/L. The geographic distribution of detections of some VOC groups, such as fumigants and oxygenates, relates to the use pattern of compounds in that group. With the exception of compounds used in organic synthesis, detection frequencies of VOCs by group are proportional to the average half-life of compounds in the group. When the organic synthesis group is excluded from the analysis, a good correlation exists between the detection frequency of VOCs by group and average half-life of compounds in the group.

Individually, VOCs were not commonly detected at an assessment level of 0.2 μg/L, with the seven most frequently detected VOCs found in only 1 to 5 percent of samples. Mixtures (two or more compounds) were a common mode of occurrence for VOCs when no assessment level was applied, and mixtures occurred in one-half of all samples that contained at least one VOC. Only 1.4 percent of samples (27 samples) had one or more VOC concentrations that exceeded a federally established drinking-water standard or health criterion. Only 0.1 percent of samples (2 samples) had one or more VOC concentrations that exceeded a taste/odor threshold.

Potential point sources of VOCs near domestic wells are numerous. Leaks from underground storage tanks and aboveground storage tanks that hold gasoline, diesel fuel, or heating oil

have the potential to be major point sources of contaminants to domestic wells. Shock chlorination may be a source of trichloromethane and other trihalomethanes in some domestic wells. Septic systems are believed to be an important source of contaminants to domestic wells, but extensive research on this subject does not exist. VOCs frequently are ingredients in household products such as cleansers and insecticides, and some VOCs have been found in septic systems.

INTRODUCTION

More than 76 billion gallons per day of ground water is withdrawn in the United States for various uses (table 1). Withdrawals for domestic (also called residential) uses that are self supplied account for about 4.4 percent of total ground-water withdrawals. Domestic uses include water used for household purposes, such as drinking, food preparation, bathing, washing clothes and dishes, flushing toilets, and watering lawns and gardens (Solley and others, 1998). Self-supplied water is withdrawn from a source by the user rather than being obtained from a public supply. As of 2002, about 40 million people in the United States receive their household water from individual private wells, and the number increases every year (Job, 2002).

Table 1. Ground-water withdrawals in the United States in 1995 by water-use category (from Solley and others, 1998)

[Mgal/d, million gallons per day]

Water-use category	Ground-water withdrawal (Mgal/d)	Percent of total ground-water withdrawal
Irrigation	49,000	64.1
Public supply[1]	15,100	19.8
Industrial	4,090	5.4
Domestic (self supplied)	3,350	4.4
Livestock	2,260	3.0
Mining	1,070	1.4
Commercial	939	1.2
Thermoelectric	565	.7
Total	76,374	100

[1] Public-supply withdrawals are withdrawn by public and private water suppliers and delivered to users for a variety of uses, such as domestic, commercial, thermoelectric power, industrial, and public water supply.

Ground water is the source of drinking water for one-half of the Nation's population and to virtually all people living in rural areas (U.S. Environmental Protection Agency, 1999a). Ground-water use for domestic purposes was approximately 26 billion gallons per day in 1995 (table 2). Of this use, about 13 percent was self supplied and 87 percent was obtained from public suppliers. Approximately 42.4 million people, or 16 percent of the U.S. population, relied on self-supplied water for domestic purposes in 1995. Nearly all of this self-supplied water was obtained from ground water (Solley and others, 1998).

Table 2. Domestic freshwater use in the United States from ground water in 1995 by water-supply category (from Solley and others, 1998)

[Mgal/d, million gallons per day]

Water-supply category	Use (Mgal/d)	Use (percent)	Population served (thousands)	Population served (percent)
Self supplied	3,350	13	42,400	16
Supplied from public suppliers	22,700	87	225,000	84
Total	26,050	100	267,400	100

Although a large number of people in the United States rely on self-supplied well water for drinking-water supply and other domestic water uses, the quality of water from these wells does not receive the same level of health scrutiny as water from public supplies. Public supplies are regulated by the U.S. Environmental Protection Agency (USEPA) and by State health or environmental departments. USEPA regulations require that public suppliers ensure that their water meets drinking-water standards, such as Maximum Contaminant Levels (MCLs), which are regulated under the Safe Drinking Water Act (SDWA) (U.S. Environmental Protection Agency, 1991, 2000a). This requirement is met by routinely testing the water for the presence of contaminants and, if needed, by treating the water to remove or reduce specific contaminants to levels that will not adversely affect human health (U.S. Environmental Protection Agency, 1999a).

The MCLs established under the SDWA apply only to community water systems (CWSs) and non-transient non-community water systems (NTNCWSs)

(U.S. Environmental Protection Agency, 1999b). A CWS is a public water system that serves at least 15 service connections used by year-round residents or regularly serves at least 25 year-round residents. A NTNCWS is a public water system that serves at least 25 of the same people over 6 months per year (U.S. Environmental Protection Agency, 1999b). This is in contrast to most self-supplied, domestic wells that generally serve only a single family (usually much less than 25 people). Because drinking-water quality from domestic wells is not regulated, owners of these wells are solely responsible for the quality of the water provided (U.S. Environmental Protection Agency, 1990a).

A primary objective of the U.S. Geological Survey's (USGS) National Water-Quality Assessment (NAWQA) Program is to characterize the quality of ambient, untreated water in the United States. In its sampling of ambient ground water, the NAWQA Program has sampled ground water from many domestic wells. Data from NAWQA's occurrence-assessment studies and from existing ambient ground-water or source-water-quality monitoring programs were analyzed for information on occurrence and status of VOCs in ground water from domestic wells.

Volatile organic compounds (VOCs) have chemical and physical properties that allow them to move freely between water and air (Bender and others, 1999). The USEPA has established MCLs in drinking water for many VOCs because of human health concerns such as short-term toxic effects and long-term chronic effects such as carcinogenicity (U.S. Environmental Protection Agency, 2000a). Because of the potential risk of some VOCs to human health, the occurrence of VOCs in water from self-supplied, domestic wells is of concern, and this concern is exacerbated by the widespread and extensive use of VOCs in households and the mobility and persistence of some VOCs in ground water.

VOCs are produced in large quantities for a multitude of uses and have been produced for a relatively long period of time. Products containing VOCs are used extensively in households (Bloeman and Burn, 1993; Bender and others, 1999) as discussed in detail later in this report. Some examples of household products that contain VOCs include cosmetics, room deodorizers, deodorants, fabric softeners, polishes, moth cakes, paint, adhesives, cleaning and polishing products, pesticides and fumigants, solvent degreasers, refrigerants, and fuels. VOCs probably have been used extensively in the past in domestic settings, and if these VOCs have sources to ground water near domestic wells the likelihood is high that VOCs will be found in ground water from domestic wells.

In addition to household use, considerable quantities of VOCs are produced and used in the United States in a variety of commercial and industrial applications, such as in fuels (gasoline, diesel fuel, etc.), dry cleaning, and the manufacture of plastics and pharmaceuticals. The production of synthetic organic chemicals, many of which are VOCs, increased by more than an order of magnitude between 1945 and 1985 (Ashford and Miller, 1991).

The production and use of VOCs in the United States results in considerable quantities of VOCs being released to the environment based on data reported in the USEPA Toxics Release Inventory (TRI) (U.S. Environmental Protection Agency, 1996, 1998). The TRI provides information on the release of toxic chemicals from manufacturing facilities in the United States. During 1996 and 1998, for example, 10 of the 20 chemicals with the largest total on-site and off-site releases to the environment were VOCs (U.S. Environmental Protection Agency, 1996, 1998). Total releases of these 10 chemicals exceeded 700 million pounds in both 1996 and 1998.

Once in the environment, many VOCs move between the atmosphere, soil, ground water, and surface water. Although many VOCs have relatively short half-lives in certain media because of degradation, other VOCs can be persistent, degrading little over a period of years, or decades. In addition, VOCs can have varying magnitudes of solubility and sorption, complicating their occurrence and transport in ground water. For example, methyl *tert*-butyl ether (MTBE), which has a high solubility in water and sorbs only weakly to soil and aquifer materials, also generally resists degradation in the anaerobic conditions usually found in ground water (Squillace and others, 1996). Thus, MTBE can persist in ground water and travel long distances through advection.

PURPOSE AND SCOPE

The purpose of this report is to provide information on the occurrence and status of VOCs at or above 0.2 μg/L (microgram per liter) in samples of ground water from rural, self-supplied domestic wells collected by NAWQA during 1986-99, or existing data compiled by NAWQA. Occurrence information is given for: (1) all VOCs as a single group, (2) seven groups of VOCs, and (3) 55 individual VOCs. Information also is presented on occurrence and status of individual VOCs and mixtures of VOCs using no assessment level. Occurrence describes the presence or absence of VOCs, detection frequencies, ranges of concentrations, and areal patterns of occurrence. Status compares VOC concentrations to federally established drinking-water standards, health criteria, and taste/odor thresholds.

Previous Investigations

Several national surveys of VOCs in drinking water in the United States have been completed. However, no national surveys are known that specifically have investigated the occurrence and status of VOCs in self-supplied, domestic well water.

The USEPA completed two national surveys between 1975 and 1981 to determine the occurrence of VOCs in finished drinking water from public supplies obtained from ground- and surface-water sources (Westrick and others, 1984; Westrick, 1990). These surveys did not address the quality of self-supplied, domestic well water.

A national survey of the occurrence and status of VOCs in untreated, ambient ground water in the conterminous United States was completed by NAWQA in 1999 using data collected during 1985-95 (Squillace and others, 1999). In that study, occurrence pertained to the incidence and location of VOCs in ground water, and status pertained to VOC concentrations relative to drinking-water standards and criteria. Ambient ground water was defined as ground water in areas where there were no known point sources of contamination prior to sampling. All VOC detection frequencies were reported at or above 0.2 μg/L, with the exception of 1,2-dibromo-3-chloropropane, which was reported at or above 1.0 μg/L. A total of 2,948 wells were used for analysis, consisting of several different types: 192 public-supply, 606 domestic, and 166 monitoring, with the remainder of the wells not having a type designation. The results of this analysis indicated that 14 percent of ground water from wells in rural areas had a detection of at least one VOC.

In 1998, the Centers for Disease Control (CDC) completed a study of the quality of water from domestic wells in nine midwestern States (Centers for Disease Control, 1998). This study followed the Mississippi valley flood of 1993, and the CDC collected samples from 5,520 households with domestic wells. The samples were analyzed for bacteria, nitrate, and atrazine but no VOCs.

In 1999, the USEPA completed an analysis of the occurrence of contaminants in public water systems (PWSs) regulated under the SDWA (U.S. Environmental Protection Agency, 1999c). Finished drinking water was analyzed in this study. Compliance-monitoring data for the SDWA were the primary data source. Data from eight States, selected to represent the national range of hydrologic regimes and pollution potential, were used to develop a national cross section of contaminant occurrence. More than 25 percent of the U.S. population using public water supplies was represented by the eight States. The results of this study indicated that VOCs commonly were detected in public drinking-water systems but exceedances of MCLs were not common.

A multi-year national and ongoing survey of MTBE and other VOCs in sources of drinking water began in 1999 by the Metropolitan Water District of Southern California, the USGS, and the Oregon Graduate Institute (Ivahnenko and others, 2001). The objective of the survey was to provide information on the frequency of detection, concentrations, and distribution of MTBE, other ether oxygenates, ether oxygenate degradation by-products, and other VOCs in sources of drinking water in the United States. The approach included a literature review and sampling of source waters for CWSs. Both randomly selected and focused ground- and surface-water sources were selected for sampling. The random sampling selected CWSs from 52 geographical entities, including the 50 States, Native American Lands, and Puerto Rico. Selection of CWSs was balanced to consider both ground- and surface-water sources. A total sample size of 954 CWSs provided information on VOC exposure from drinking water for an estimated 80 million people. Approximately 140 source waters were selected for a focused source-water sampling. Source waters selected for the focused survey were those known or suspected to be susceptible to gasoline contamination. Approximately 80 of these 140 source waters were ground-water sources. The results of this study indicated that VOCs were commonly detected in sources for CWSs but were more frequently detected in the focused sources compared to the randomly selected sources.

An assessment of the occurrence of MTBE and other VOCs in drinking water in the northeast and mid-Atlantic regions of the United States was completed in 2000 (Grady and Casey, 1999, 2001; Moran and others, 2001). The assessment summarizes information on the quality of drinking water obtained from SDWA compliance-monitoring data for 2,110 randomly selected CWSs in the 12 States included in that study (Grady and Casey, 2001). Water-quality data included more than 21,000 chemical analyses of VOCs in drinking-water samples collected during 1993-98. The results of this study indicated that 39 percent of the 2,110 CWSs reported a detection of one or more VOCs at or above 1.0 µg/L.

At least two States have conducted statewide studies and possibly other States have conducted studies of the occurrence and status of VOCs in self-supplied, domestic well water. These statewide studies are summarized briefly below.

Maine

In 1998, the State of Maine conducted a statewide, statistically based study of the occurrence of MTBE, benzene, toluene, ethylbenzene, and xylenes (BTEX) in drinking water (State of Maine, 1998). Sampled drinking-water supplies included 951 randomly selected household sources (919 wells, 23 springs, and 9 lakes) collectively grouped together as wells in the report. Also sampled were 793 of the 830 regulated CWSs and NTNCWSs in the State. The laboratory reporting level for all compounds except total xylenes was 0.1 µg/L. The laboratory reporting level for total xylenes was 0.3 µg/L. MTBE was detected in 150 of the 951 household wells (15.8 percent). Concentrations of MTBE in 1.1 percent of the wells were greater than the State's drinking-water standard of 35 parts per billion.

Extrapolated statewide, this percentage translates to an estimated 1,400 to 5,200 private wells in Maine with concentrations of MTBE that may exceed the drinking-water standard (State of Maine, 1998). MTBE concentrations were less than 1 part per billion in 92.3 percent of the sampled household wells, and between 1 and 35 parts per billion in 6.6 percent of the wells. Compared to MTBE, other gasoline compounds were detected infrequently, and concentrations of BTEX compounds were well below drinking-water standards. Both the location of the water supply in areas of reformulated gasoline (RFG) use and high population density were associated with detectable concentrations of MTBE. Factors that were found not to be associated with MTBE detections included type of well or water supply and the proximity to gasoline storage tanks.

Wisconsin

The State of Wisconsin, Department of Natural Resources, has been testing for VOCs in well water since 1982 and has completed sampling of all community wells, surface-water sources, and about 1,500 non-community public and private wells (Wisconsin Department of Natural Resources, 1998). Of the 1,500 non-community public and private wells tested, 355 (or 24 percent) had at least one detection of a VOC. Many of the private wells were selected for sampling because they were considered to be especially vulnerable to contamination, were near other contaminated wells, or were delivering water with objectionable tastes or odors (Wisconsin Department of Natural Resources, 1998). Therefore, detections of VOCs might be higher than detections resulting from a random selection of private wells throughout Wisconsin.

Study Approach

An extensive and representative inventory of available water-quality data is required to determine the occurrence and status of VOCs in ground water from rural, self-supplied, domestic wells in the United States. The sources of data and the procedures and criteria used in selecting data for analysis are described in this section. The VOC data used for analysis in this report were compiled from two sources: (1) untreated water from rural, self-supplied domestic wells sampled by NAWQA personnel and water samples analyzed at the USGS National Water-Quality Laboratory (NWQL) between 1993 and 1999 as part of NAWQA's occurrence-assessment studies; and (2) untreated water from rural, self-supplied, domestic wells collected and analyzed as part of ambient ground-water or source-water-quality monitoring programs conducted by local, State, and other Federal agencies between 1986 and 1995. In both data sources, water samples were collected at the wellhead prior to treatment or storage. Only wells in rural areas were selected in order to examine the quality of water in domestic wells. A rural area is defined as having a population density of less than 386 persons/km^2 (1,000 persons/mi^2 or 1.56 persons/acre). Too few wells have been sampled to characterize the occurrence of VOCs in domestic wells in urban areas.

NAWQA Ground-Water Occurrence-Assessment Studies

In 1991, the NAWQA Program began full-scale implementation. The long-term goals of the NAWQA Program are to describe the status and trends in the quality of a large representative part of the surface-water and ground-water resources of the United States and to provide an improved understanding of the primary natural and human factors that affect the quality of these resources. The NAWQA Program has two major operational components (Gilliom and others, 1995): (1) hydrologic investigations of large river basins and aquifer systems, referred to as Study-Unit Investigations; and (2) national synthesis assessments that summarize results from NAWQA studies with information from other programs, agencies, and researchers to produce regional and national assessments for priority water-quality issues. National synthesis assessments of nutrients and pesticides began in 1991, a synthesis of VOCs began in 1994, and syntheses of trace elements and ecology began in 1999. This report is a product of the VOC national synthesis assessment.

NAWQA ground-water occurrence-assessment studies, as part of the hydrologic investigations of Study Units, include a broad characterization of water quality in one or more aquifers underlying each Study Unit (Gilliom and others, 1995). Aquifers selected for this characterization generally are those with the largest withdrawals for water supply in each Study Unit. The characterization of water quality in each aquifer is achieved by sampling a network of spatially distributed, randomly selected existing wells throughout the aquifer. Each network consists of about 30 wells. Domestic wells are selected preferentially over other types of wells, if available, provided that the spatially distributed, randomly selected network design is maintained. In the NAWQA data used for analysis in this report, the majority of wells were sampled as a part of these types of assessments.

Study Units also conduct studies to determine the relation between shallow ground-water quality and overlying land use (Gilliom and others, 1995). Networks of wells within areas of specific types of land use (for example, agricultural or urban uses) and that are screened or open at or near the water table are sampled for these studies. In contrast to the studies of major aquifers, sites to be sampling for the land-use studies were required to have a minimum of 50 percent of the targeted land use within a ¼-mile radius of the well. Most of the wells for these studies are monitoring wells installed by the NAWQA Study Units; however, some other types of wells, possibly including domestic wells, also might be sampled if the cost of installing monitoring wells is prohibitive. In the NAWQA data used for analysis in this report, some of the wells were sampled as part of the agricultural land-use studies.

Samples collected as part of the NAWQA Program consist of untreated water because the primary objective of NAWQA ground-water occurrence and status assessments is to characterize the quality of the ground-water resource, not the quality of treated or finished drinking water. To meet this objective, samples of finished water are not collected because the quality of finished drinking water may not be a valid measure of the quality of the ground-water resource. Finished water may be a blend of water from various sources, including both ground and surface water. Even if the source water is derived only from ground water, the quality of the finished water (after blending) might vary depending on which wells were being pumped and the relative rates of pumping from those wells (Squillace and others, 1999). In addition, VOC concentrations might increase or decrease during water treatment and distribution.

As of 2001, about 4,600 wells had been sampled by NAWQA Study Units as part of the studies described above. Details about network design, well selection, sampling protocols, and other data-collection requirements for NAWQA Study-Unit ground-water investigations are described in Scott (1990), Gilliom and others (1995), Koterba and others (1995), Lapham and others (1995), and Koterba (1998). A minimum amount of information about a well generally must be known and entered into the USGS National Water Information System (NWIS) Ground-Water Site Inventory (GWSI) database (Maddy and others, 1989) before a well is selected by NAWQA for water-quality sampling. In addition to the minimum requirements, other existing data for each well are compiled and entered into the GWSI database.

Sampling protocols for ground-water samples collected by NAWQA for VOC analysis consist of collecting an unfiltered sample in a 40-mL amber glass vial from each well after purging a minimum of three well volumes. Completion of well purging is determined from evaluation of stability of field measurements of water temperature, specific conductance, dissolved oxygen, pH, and alkalinity (Koterba and others, 1995). Samples are collected using polytetrafluoroethylene tubing connected to a spigot on each well as close as possible to the wellhead and prior to water treatment and pressure or holding tanks (Lapham and others, 1995). Samples are collected in a sample-collection chamber designed to isolate the sample from potential contamination by VOCs in the atmosphere and from other possible sources of VOCs, such as emissions from nearby motor vehicles and generators (Wilde and others, 1999). Each vial is allowed to overflow, preserved with one to five drops of 1:1 hydrochloric acid to pH 2, and then capped leaving no headspace. If there was evidence of air bubbles in the vial after the sample was preserved and capped, the sample was discarded and a new sample was collected in a new vial.

All sampling equipment in contact with a water sample, including sampling tubes, is cleaned between sampled wells. Cleaning is accomplished by circulating a non-phosphate detergent in a tap water solution through the equipment, and then rinsing the equipment successively with tap water, methanol, and deionized water (Koterba and others, 1995). All equipment is wrapped in either aluminum foil or clear plastic for storage.

The method of analysis for VOCs in NAWQA-collected samples is purge and trap gas chromatography/mass spectrometry (GC/MS) (Rose and Schroeder, 1995; Connor and others, 1998). The analytical schedule used from 1993 to April 1996 by the NAWQA Program included 60 VOCs. The NWQL used a custom analytical method from April 1996 to October 1996, and the current analytical schedule was used after October 1996. The methods used since April 1996 include analyses for 86 VOCs plus a search for nontarget analytes. The laboratory reporting level for each VOC using schedules prior to April 1996 generally was 0.2 µg/L. The laboratory reporting levels for newer methods generally are about one-half an order of magnitude lower than those for older methods because of new, long-term approaches for determining method detection levels (Oblinger Childress and others, 1999). The laboratory reporting levels for analytes in the newer schedules also are variable between different VOCs and can vary throughout time for individual compounds (Oblinger Childress and others, 1999).

As of 1999, 55 VOCs were selected by the NAWQA Program for emphasis and are considered national target analytes (Bender and others, 1999). These include 21 halogenated alkanes, 10 halogenated alkenes, 3 aromatic hydrocarbons, 9 alkyl benzenes, 6 halogenated aromatics, 4 ethers, 1 aldehyde, and 1 nitrile (Bender and others, 1999). Only these 55 VOCs are examined in this report because of the emphasis given to them in the NAWQA Program. A list of target analytes, by compound use group, is presented later in this report. Concentrations of 1,3-dimethylbenzene (*m*-xylene) and 1,4-dimethylbenzene (*p*-xylene) are reported as the sum of these two isomers by NWQL because they cannot be separated by current GC/MS methods (Bender and others, 1999). Also, 2-propenal was deleted from the NWQL schedules in May 1998 because of erratic and poor instrument response after a new concentrator was installed. Nevertheless, results for 2-propenal are included in this report because the NAWQA Program collected acceptable data during 1996-98 (Bender and others, 1999). Of the 55 VOCs, 29 have federally established MCLs, 28 are classified as known, probable, or possible human carcinogens, 35 have potential non-carcinogenic human health effects but currently do not have national regulations (Drinking Water Equivalent Level (DWEL) or Lifetime Health Advisory (HA)), and 33 have documented taste/odor thresholds (Bender and others, 1999).

Prescribed, consistent quality-assurance (QA) procedures are followed in the field and in the laboratory for NAWQA studies. QA procedures in the field include standard, written protocols for purging wells, collecting field measurements, collecting VOC samples, cleaning equipment (decontamination) after each visit to a well, and collecting quality-control (QC) samples (Koterba and others, 1995).

QC samples for VOCs include a variety of types and generally comprise about 10 to 15 percent of the samples collected. The review of QC data collected by NAWQA indicated that a small number of samples were subject to random contamination resulting from collection, handling, shipping, processing, and/or analyses. However, the majority of samples showed no systematic contamination on a national basis (G.C. Delzer, U.S. Geological Survey, written commun., 2001). If the QC data indicated evidence of systematic contamination, the associated environmental data were coded to indicate the possibility of contamination and these data were not used in subsequent analyses (G.C. Delzer, U.S. Geological Survey, written commun., 2000).

Local, State, and Other Federal Water-Quality Monitoring Programs

NAWQA sampling does not cover all areas of the United States. However, some local, State, and other Federal agencies sample domestic and other types of wells for VOCs as part of ambient ground-water or source-water-quality monitoring programs. To augment the NAWQA data, VOC data from some of these monitoring programs have been compiled (Lapham and others, 1997). These data are referred to as retrospective data. The locations where retrospective VOC data were compiled included areas in NAWQA Study Units that had not been sampled at the time of the data compilation and areas outside of the NAWQA Study Units. VOC data from approximately 15,500 wells from 43 ambient monitoring programs or well networks in 27 States had been compiled as part of this retrospective effort as of August 1997 (Lapham and others, 1997). As of summer 2001, data from an additional 1,283 wells had been compiled. VOC data collected by local, State, and other Federal agencies were selected only if they met specific criteria in terms of monitoring objectives, network design, well construction, and methods of sample collection and laboratory analysis (table 3). These criteria were followed to help ensure consistency between the NAWQA and retrospective data.

Table 3. General criteria for well-network design, well construction, and data selection used when compiling retrospective data from local, State, and other Federal agencies (modified from Lapham and Tadayon, 1996)

[VOC, volatile organic compound; µg/L, micrograms per liter]

Category of criteria	Description of criteria
Well-network design	Wells are suitably located in relation to the desired spatial and depth design.
	All wells or a subset of wells from one or more well networks collectively result in a generally unbiased, random, equal-area distribution of sampling sites throughout the aquifer or part of the aquifer of interest.
Well construction	Well-construction information is sufficient to ensure that the water level measured in the well represents the water level in the aquifer and that the sample water collected is from that aquifer.
	Ideally, the well construction and pumping equipment in the well do not affect concentrations of VOCs in the water sample.
Data selection	National methods for collection and analysis of VOCs are used. The analytical method and method detection limits or the reporting levels for each VOC analyte are known and are less than about 5 µg/L.
	Analysis is done by a laboratory certified by the U.S. Environmental Protection Agency.
	The location of the well from which the sample is collected is known by latitude and longitude.
	The sample is collected from untreated (source) water.
	The water sample is collected at or near the wellhead before being held in a pressure or holding tank.
	The analyte name is identified by parameter code (P-code), and the analyte concentration is known.
	The date (at a minimum, the year) of sample collection is known. (In general, the latest measured concentration of the analyte from a well after January 1, 1985, is used; however, in some cases this criteria might not apply, as discussed in Lapham and Tadayon (1996)).
	Quality-control data are used to evaluate and, if necessary, to censor and/or codify the environmental data prior to its compilation at a national level to the extent that quality-control data are available.

Field and laboratory methods and QA procedures followed for the collection and laboratory analysis of the retrospective data were documented in a general way when the data were compiled. This approach ensured that, to the extent possible, all data met a minimum standard of quality. Accordingly, only data that met the specific selection criteria listed in table 3 were selected. All retrospective data should meet the following critical QA requirements: national methods for collection and analysis of VOCs were used; the analytical method and method detection limits or the reporting levels for each VOC analyte were known and are less than about 5 µg/L; analyses were done by a laboratory certified by the USEPA; and QC data were used, to the extent they were available, to evaluate and censor and/or codify, if necessary, the environmental data prior to its compilation at a national level.

Selection of VOC Data

NAWQA and retrospective VOC data had to meet the requirements listed in table 4 to be included in the analyses for this report. Many types of wells including domestic, public supply, monitoring, and others were sampled by both NAWQA and other agencies conducting water-quality monitoring; however, only domestic wells were included for analyses in this report. For some samples, particularly in the retrospective data set, information such as type of well was not documented, and these samples were omitted from the data set. Other missing information about a well resulted in the elimination of additional data. The general limitations imposed by lack of supporting information about each well diminishes the usefulness of some of the retrospective data in this analysis, and this is discussed in more detail in Lapham and others (1997) and Lapham and others (2000).

Table 4. Criteria used to select VOC data for analysis

[VOC, volatile organic compound; NAWQA, National Water-Quality Assessment Program; SU, study unit; km, kilometer; >, greater than; ≤, less than or equal to; µg/L, micrograms per liter; NWQL, U.S. Geological Survey National Water-Quality Laboratory]

Study objective	National occurrence and status assessment of one or more VOCs, groups of VOCs, and individual VOCs.
Data sources	1991 and 1994 NAWQA SU data and retrospective data.
Sampling period	1986 through 1999 (generally, the most recent sample from the well).
Well type	Wells used for domestic water supply in rural areas.[1]
Sample collection point	At the wellhead.
Sample type	Untreated water (collection prior to water treatment and pressure or holding tanks).
Target analytes	As many of 55 VOCs as possible (the number of VOCs in each analysis might differ, but a minimum of 24 VOCs were required).[2,3]
Other criteria	Well spacing >1 km.[4] Only one sample from each well. The laboratory reporting levels for each VOC in the sample generally was ≤ 0.2 µg/L.

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[1] Rural areas are areas with a population density less than 386 people per square kilometer.

[2] 55 VOCs were selected for emphasis in the NAWQA Program. However, concentrations of 1,3-dimethylbenzene (*m*-xylene) and 1,4-dimethylbenzene (*p*-xylene) are reported together by the NWQL because these isomers cannot be separated by the gas chromatography/mass spectrometry method (Bender and others, 1999). Therefore, concentrations for only 54 analytes are reported. 2-propenal was deleted from the NWQL schedules in May 1998 because of erratic and poor instrument response after a new concentrator was installed. However, this VOC is included as a VOC target analyte because 2½ years of acceptable data were collected by the NAWQA Program in 1996-98 (Bender and others, 1999, p. 9).

[3] The list of VOCs is provided later in this report in table 6.

[4] Well spacing is greater than 1 km to avoid spatial autocorrelation between samples.

The NAWQA and retrospective data sets combined contain VOC analyses from 2,479 samples of ground water from domestic wells. Only one primary environmental sample from each domestic well was analyzed in this report. Because each well had only one environmental sample analyzed, the words "well" and "sample" will be used interchangeably from this point on. If the type of well was not identified, the well was not selected. Only a subset of 1,926 samples met five additional selection criteria required for inclusion in data analysis. The five selection criteria used include: (1) limiting the location of the well to a rural area; (2) limiting each well to only one water sample; (3) specifying the number of VOCs included in the laboratory analysis of the water sample; (4) specifying minimum laboratory reporting levels for the majority of analytes; and (5) specifying a minimum separation distance between wells (table 4).

Only domestic wells located in rural areas were selected to avoid any potential bias that might be associated with population density. Higher population density in the vicinity of a well has been shown to be strongly associated with a higher probability of detecting VOCs (Squillace and others, 1999). Because only 4 percent of wells were located in urban areas, only a small amount of data was eliminated. The population density associated with each well was interpolated between grid cells that were entirely or partly within the 1-km radius of each well. Urban wells were identified and removed if the population density within a 1-km radius of the well was greater than 386 people/km^2; a population density of 386 people/km^2 or more is considered urban (Hitt, 1994). Population-density data were available as a geographic information system grid from the Consortium for International Earth Science Information Network (1996). This step removed 91 samples from the data set.

Only one sample from each well was selected (table 4). Removal of duplicate samples was necessary in order to accurately describe occurrence of VOCs in the ground-water resource. Computing occurrence with a varying number of samples per well does not provide an accurate picture of water quality by well. Removal of duplicate samples eliminated 129 samples from the data set. Generally, the sample used for analysis from each well was the one with the most recent sampling date. In the case of NAWQA data, the sample selected for analysis was the one classified as the primary environmental sample for the well. If there was a choice of samples collected by NAWQA and a local, State, or other Federal monitoring program, samples collected by NAWQA were selected. Data from NAWQA samples were preferred to data from other sources because the number of VOCs measured by NAWQA (55 VOCs) usually is larger than that measured by other monitoring programs. In addition, documented and consistent field sampling methods and laboratory analyses are used in NAWQA data collection that minimizes potential data bias and variability.

The third step in the selection process was to limit the data set to only those samples that included analyses for at least 24 VOCs. Samples collected by NAWQA had analyses for at least 55 VOCs, and results for 55 VOCs are included in this report. However, the number of VOCs analyzed in each well or network in the retrospective data set varied considerably. Therefore, the purpose of this third step was to ensure, to the extent possible, that all wells had analyses for a relatively large number of VOCs. A minimum number of 24 VOCs was selected as a threshold value after the distribution of the number of VOCs analyzed in each sample was examined. Then comparisons of frequencies of detections among VOCs would be based on approximately the same number of analyses for each VOC. This step removed 137 samples from the data set.

The fourth step was to select only those samples for which the laboratory reporting levels for each VOC in the sample generally were less than or equal to 0.2 μg/L. The level of 0.2 μg/L was chosen because this concentration is the most frequently occurring reporting level in the data set. This step was performed because large numbers of analytes with high reporting levels can potentially bias detection frequencies low. In order to avoid this, only samples that had at least 75 percent of all reporting levels at or below 0.2 μg/L were retained. This step removed 138 samples from the data set.

Finally, a fifth step in data selection was completed to avoid potential bias in computing detection frequency and potential problems with spatial autocorrelation. Spatial autocorrelation is caused when wells are too closely spaced and thus do not provide sample independence (Barringer and others, 1990). This can cause inaccuracy and inefficiency in tests relating occurrence of water-quality indicators to variables such as land use (Barringer and others, 1990). Barringer and others (1990) have shown that wells separated by a distance of less than 1 km show distinct autocorrelation with respect to cropland use. Spatial autocorrelation also could potentially cause bias in the computation of detection frequencies for water-quality constituents.

In order to prevent spatial autocorrelation and potential bias in detection frequency, each well in the data set was separated from other wells by at least a 1-km distance. An algorithm preferentially eliminated wells that were within the separation distance. Wells sampled by NAWQA were retained if there was a choice to select NAWQA-sampled wells versus retrospective wells. This step removed an additional 58 samples from the data set.

After these five selection steps, the final data set consisted of 1,926 samples. Of these samples, 1,325 were samples collected by NAWQA and 601 were samples collected by local, State, and other Federal agencies in other ambient ground-water or source-water-quality monitoring programs (table 5). Other general characteristics of the data set used in this report are described in table 5.

Statistical Methods in Data Analysis

To better understand the significance of some of the analytical results and the hydrologic processes that may have caused these results, statistical tests were performed to evaluate and compare groups of data. Two statistical tests were performed: (1) the Spearman correlation test for determining correlation between two continuous variables, and (2) Pearson's chi-square test of independence for determining dependence between two categorical variables where both variables are nominal.

The Spearman correlation test was performed to determine both the correlation between detection frequency of one or more VOCs by State and the number of wells sampled by State (Occurrence and Status - All Samples section) and correlation between detection frequency of VOCs by group and average half-life (Occurrence and Status - Detections of VOCs by Group section). The null hypothesis for this test states that there is no correlation between the two variables (Helsel and Hirsch, 1992). If the null hypothesis is rejected, then an association exists between the two variables at the specified statistical significance level. The computed statistic for this test is referred to as rho. The *p*-value is the probability that rejection of the null hypothesis is wrong or the probability of committing a Type I error (Sheskin, 1997).

The Pearson's chi-square test of independence was performed to determine if detection frequency of one or more VOCs is dependent on well type for domestic versus public supply wells (Occurrence and Status - Geographic Distribution section). The null hypothesis for this test states that there is no dependence of one variable (detection frequency) upon the other (well type) (Helsel and Hirsch, 1992). If the null hypothesis is rejected, then the value of one variable is dependent upon the other. Again, the *p*-value is the probability that rejection of the null hypothesis is wrong or the probability of committing a Type I error (Sheskin, 1997).

Table 5. General characteristics of the NAWQA and retrospective data used for analysis in this report

[NAWQA, National Water-Quality Assessment Program; VOC, volatile organic compound]

General Information	
Number of domestic wells	1,926
Number of domestic wells sampled by NAWQA	1,325
Number of domestic wells sampled in other monitoring programs (retrospective data)	601
Number of States covered	39
Sampling period	1986-99
VOC Analyses	
Range in the number of VOCs analyzed per sample	24 to 55
Range in the reporting level, in micrograms per liter	0.012 to 1,000
Well Characteristics	
Range in depth of wells, in feet below land surface	6 to 1,500
Median depth of wells, in feet below land surface	140
Lithologic Information	
Percentage of wells screened in unconsolidated aquifers	34
Percentage of wells screened in or open to consolidated aquifers	47
Percentage of wells for which lithologic information was not recorded	19

The statistical significance level is the accepted level of probability of committing a Type I error (Sheskin, 1997). In both statistical tests for this study, the statistical significance level (α) used was 0.05. If the p-value associated with a statistical test is less than the statistical significance level, the null hypothesis is rejected. If the p-value associated with a statistical test is greater than or equal to the statistical significance level, the null hypothesis is not rejected.

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OCCURRENCE AND STATUS

Six major topics related to the occurrence and status of VOCs in ground water from rural, self-supplied, domestic wells are presented. These six topics are: (1) detections of at least one VOC at an assessment level of 0.2 µg/L; (2) detections of VOCs by predominant use group at an assessment level of 0.2 µg/L; (3) detections of individual VOCs at an assessment level of 0.2 µg/L; (4) status of VOC concentrations; (5) detections of VOCs using no assessment level; and (6) detections of mixtures of VOCs using no assessment level. The VOC analytes targeted in this study, by predominant use group, are presented in table 6. The total sample size varies between individual VOCs because not every sample from the retrospective data was analyzed for all 55 target VOCs. The number of VOCs analyzed in a sample ranged from 24 to 55 (table 5). Analytical results for 1,3-dimethylbenzene and 1,4-dimethylbenzene are reported as the sum of concentrations for the two compounds by the NWQL; therefore, the number of target analytes with reported concentrations used for occurrence and status in this report is 54.

A uniform assessment level of 0.2 µg/L was chosen for analyses in some of the following sections, and the basis for this strategy will be explained in more detail. The assessment level should be distinguished from the laboratory reporting level. The laboratory reporting level is a level of censoring, or lack of censoring, that is applied at the analytical laboratory prior to the data being released. A detailed discussion of laboratory reporting levels is beyond the scope of this report but can be found in Oblinger Childress and others (1999). An assessment level is a level of censoring applied to water-quality data that have variable laboratory reporting levels either between subsets of VOC analytes or between individual VOC analytes. The assessment level is applied to data received from the laboratory and is subsequent to the laboratory reporting level. The primary purpose of the assessment level is for accurate comparison of detection frequencies between subsets of VOC analytes or between individual VOC analytes.

Because detection frequency is strongly dependent on the assessment level, comparisons of detection frequencies between groups of VOCs or between individual VOCs may not reflect true differences in water quality if the laboratory reporting level varies between VOCs. Most VOCs analyzed by NAWQA since April 1996 have variable laboratory reporting levels. The different laboratory reporting levels are based on the differing responses of compounds to the analytical instrumentation, and many compounds have laboratory reporting levels that vary as method changes are implemented or new instrumentation is used (Oblinger Childress and others, 1999). For retrospective data, the laboratory reporting levels also are quite variable between compounds, and this variability is most likely due to differing laboratory censoring criteria.

The procedure used to establish a uniform assessment level applied to every analysis in every sample and only applied to quantified concentrations. For example, if a VOC in a sample had a detectable concentration of 0.1 µg/L and an analysis was done at an assessment level of 0.2 µg/L, then the reported concentration for that VOC in that sample was censored to less than 0.2 µg/L (a non-detection). Detectable concentrations equal to or greater than 0.2 µg/L were unaltered.

Table 6. Grouping of VOCs by predominant use

Fumigants	Gasoline hydrocarbons	Organic synthesis	Oxygenates	Refrigerants	Solvents	Trihalomethanes
Bromomethane	Benzene	Bromoethene	*tert*-Amyl methyl ether	Chloromethane	Chlorobenzene	Bromodichloromethane[1]
1,2-Dibromo-3-chloropropane	*n*-Butylbenzene	Chloroethene	Diisopropyl ether	Dichlorodifluoromethane	Chloroethane	Dibromochloromethane[1]
1,2-Dibromoethane	1,2-Dimethylbenzene	1,1-Dichloroethene	Ethyl *tert*-butyl ether	Trichlorofluoromethane	1,2-Dichlorobenzene	Tribromomethane[2]
1,4-Dichlorobenzene	1,3-Dimethylbenzene[3]	Ethenylbenzene	Methyl *tert*-butyl ether	1,1,2-Trichloro-1,2,2-trifluoroethane	1,3-Dichlorobenzene	Trichloromethane[2]
cis-1,3-Dichloropropene	1,4-Dimethylbenzene[3]	Hexachlorobutadiene			1,1-Dichloroethane	
trans-1,3-Dichloropropene	Ethylbenzene	(1-Methylethyl)benzene			1,2-Dichloroethane	
	Methylbenzene	2-Propenal			*cis*-1,2-Dichloroethene	
	Naphthalene	2-Propenenitrile			*trans*-Dichloroethene	
	1,2,4-Trimethylbenzene	1,2,3-Trichlorobenzene			Dichloromethane	
					1,2-Dichloropropane	
					Hexachloroethane	
					n-Propylbenzene	
					Tetrachloroethene	
					Tetrachloromethane	
					1,2,4-Trichlorobenzene	
					1,1,1-Trichloroethane	
					1,1,2-Trichloroethane	
					Trichloroethene	
					1,2,3-Trichloropropane	

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[1] Although classified as a trihalomethane, is used predominantly in organic synthesis.

[2] Although classified as a trihalomethane, is used predominantly as a solvent.

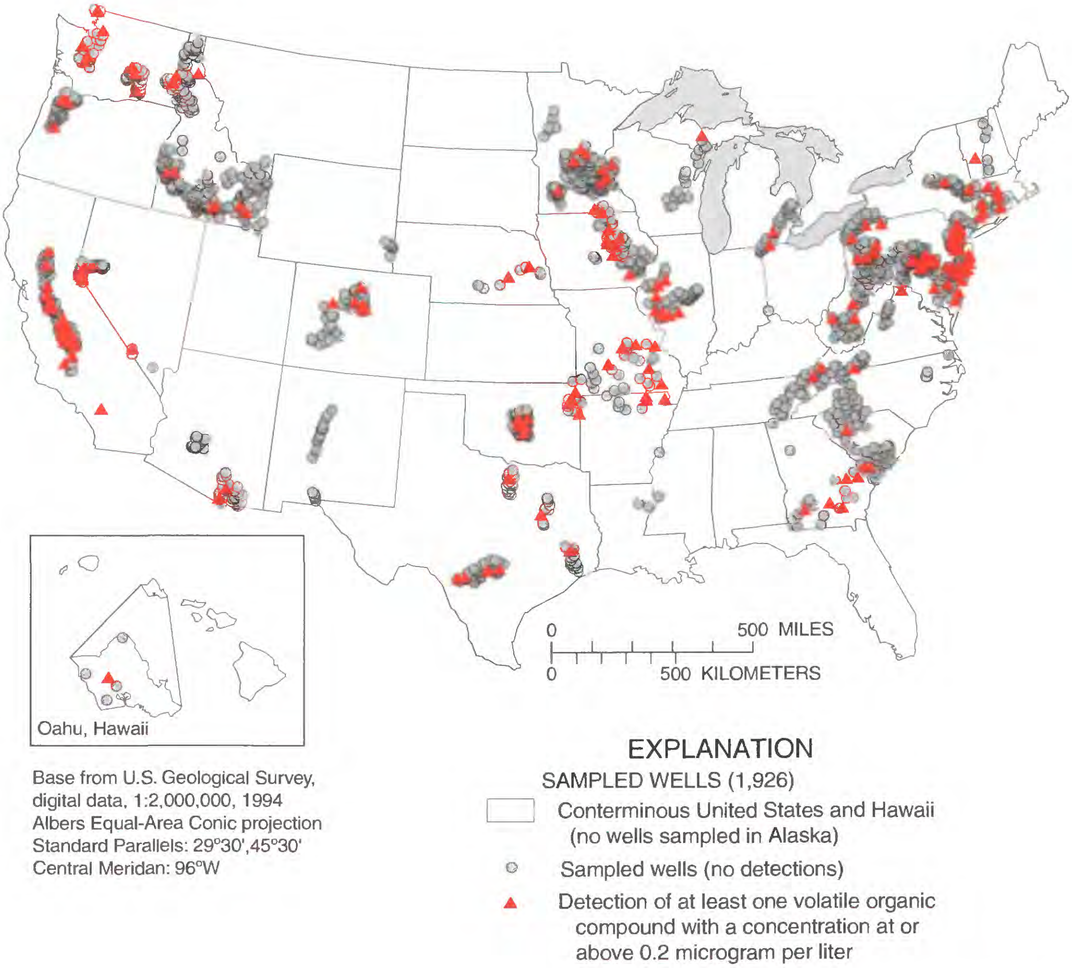
[3] Analytical results reported as the sum of concentrations for these two compounds by U.S. Geological Survey National Water-Quality Laboratory.

Detections of at Least One VOC at an Assessment Level of 0.2 microgram per liter

Samples of untreated water from 1,926 rural, self-supplied domestic wells (fig. 1) were analyzed to determine the national occurrence and the distribution of at least one VOC. Detection frequencies are reported at an assessment level of 0.2 µg/L. Three sets of results are presented: (1) detection frequencies of at least one VOC from all 1,926 samples; (2) detection frequencies for the subset of samples that contained VOCs; and (3) the areal distribution of VOC detections, nationally and by State.

All Samples

Detection frequencies for at least one VOC were computed at an assessment level of 0.2 µg/L. Most samples contained no VOCs at or above a concentration of 0.2 µg/L. No VOCs were detected at or above 0.2 µg/L in 1,694 of the 1,926 samples, or about 88 percent. Conversely, one or more VOCs were detected in 232 of the 1,926 samples, or about 12 percent (table 7). This detection frequency is relatively low compared to the 26-percent detection frequency of one or more VOCs in public supply wells sampled by the NAWQA program from 1993-2000 at an assessment level of 0.2 µg/L (2002 analysis of



Base from U.S. Geological Survey, digital data, 1:2,000,000, 1994
Albers Equal-Area Conic projection
Standard Parallels: 29°30',45°30'
Central Meridan: 96°W

Figure 1. Location of rural, untreated, self-supplied domestic wells that were sampled for this study, and the location of wells where at least one volatile organic compound was detected at an assessment level of 0.2 microgram per liter.

current NAWQA data). These results are statistically different at a significance level of $\alpha = 0.05$ ($p = 0$; chi-square independence test). The higher detection frequency in public supply wells compared to domestic wells may be due, in part, to the higher pumping rates, pumping stress factors, and larger contributing areas of public supply wells.

Samples that Contained VOCs

For the samples in which one or more VOCs were detected, the detection frequency of VOCs in samples decreases as the number of VOCs detected increases (fig. 2). Seventy-two percent of the 232 samples (8.7 percent of all 1,926 samples) in which one or more VOCs were detected contained only one VOC. Twenty-eight percent of the samples that had a detection of at least one VOC had two or more VOCs detected (table 7). Three VOCs were detected in about 6 percent of 232 samples. Only about 5 percent of 232 samples contained 4 or more VOCs.

Areal Distribution of VOC Detections, Nationally and by State

The 232 samples with detections of at least one VOC in rural, self-supplied, domestic wells occur throughout the conterminous United States and Hawaii (fig. 1). Explaining the observed areal distribution of VOCs in domestic well water is problematic for several reasons. One reason is that the compounds that are detected differ from well to well. Another reason is that the most important sources of VOCs, the compounds being released, and the amounts entering ground water likely differ in different areas of the United States. The distribution of these sources across the United States is not well documented. For example, fumigants might be the most important VOC source in agricultural areas.

Most of the States where domestic wells were sampled had at least one sample in which one or more VOCs were detected (fig. 1; table 8). Overall, samples with detections of at least one VOC were collected from wells located in 31 of the 39 States. The most frequent detections of at least one VOC occurred in New Jersey where one or more VOCs were detected in 44 of the 97 wells sampled. California had detections of at least one VOC in 39 of the 132 wells sampled in that State (table 8). Detection frequencies by State are presented in table 8 only for those States in which there were at least 30 wells sampled. A sample size of 30 was considered to be a minimum sample size for calculation of detection frequency for this report. Bias in the detection frequency by State might be expected because of the variability in the numbers of domestic wells sampled by State; however, a strong correlation does not exist between the number of wells sampled per State and detection frequency of one or more VOCs (Spearman's rho = -0.127, $p = 0.616$).

Table 7. Percent detections of at least one volatile organic compound in untreated water from 1,926 wells at an assessment level of 0.2 microgram per liter

[VOC, volatile organic compound; >, greater than; N, number of samples]

VOC occurrence	Number of samples with indicated occurrence	Percent detection from samples that contained at least one VOC [N = 232]	Percent detection from all samples [N = 1,926]
>5 VOCs detected	3	1	0.2
5 VOCs detected	5	2	0.3
4 VOCs detected	4	2	0.2
3 VOCs detected	13	6	0.7
2 VOCs detected	40	17	2.1
1 VOC detected	167	72	8.7
At least one VOC detected	232	100	12
No VOCs detected	1,694	Not applicable	88

Table 8. Distribution of samples, by State, with a detection of at least one volatile organic compound at an assessment level of 0.2 microgram per liter

[NC, not computed; VOC, volatile organic compound]

State	Number of samples analyzed	Number of samples with one or more VOCs detected	Frequency of detection (percent)
States with Samples from Greater Than or Equal to 30 Wells			
Arizona	71	2	3
California	132	39	30
Colorado	54	8	15
Iowa	57	7	12
Idaho	287	7	2
Illinois	52	8	15
Minnesota	173	8	5
Missouri	30	7	23
New Jersey	97	44	45
Nevada	73	8	11
New York	53	2	4
Oklahoma	94	8	9
Oregon	56	4	7
Pennsylvania	164	20	12
South Carolina	48	3	6
Texas	96	8	8
Washington	88	13	15
West Virginia	39	4	10
States with Samples from Less Than 30 Wells			
Arkansas	12	4	NC
Connecticut	12	6	NC
Delaware	8	2	NC
Georgia	22	5	NC
Kansas	1	0	NC
Louisiana	2	0	NC
Massachusetts	6	2	NC
Maryland	11	2	NC
Michigan	29	3	NC
Mississippi	2	0	NC
North Carolina	21	1	NC
Nebraska	9	2	NC
New Hampshire	3	0	NC
New Mexico	22	0	NC
Ohio	6	0	NC
Rhode Island	1	0	NC
Tennessee	26	1	NC
Virginia	29	1	NC
Vermont	3	1	NC
Wisconsin	28	2	NC
Wyoming	9	0	NC
Total	1,926	232	NC

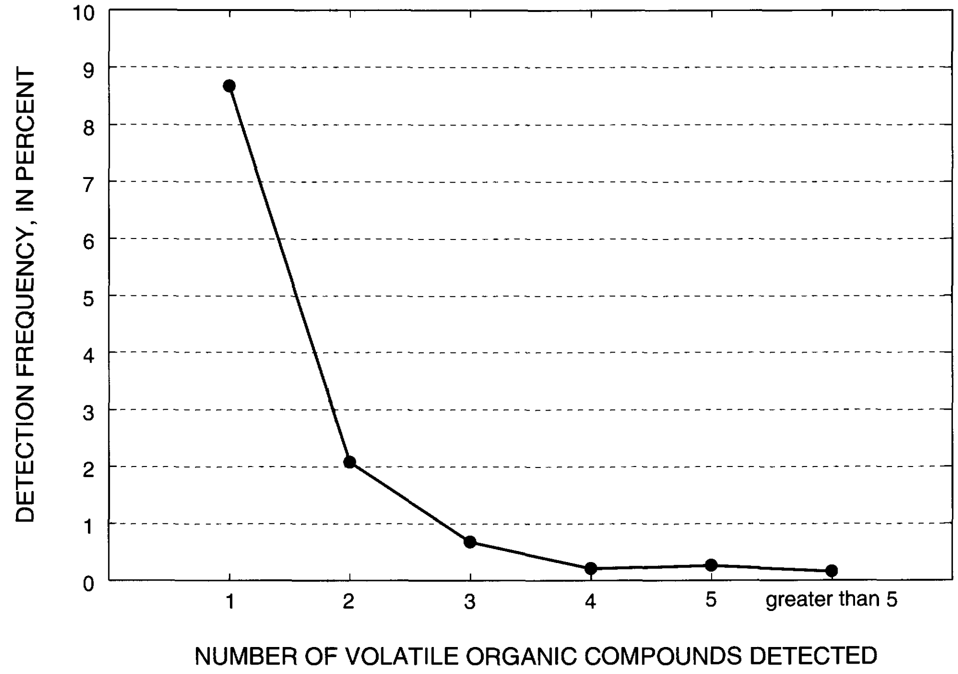


Figure 2. Detection frequency versus number of volatile organic compounds detected at an assessment level of 0.2 microgram per liter.

The eight States in which no VOCs were detected were Kansas, Louisiana, Mississippi, New Hampshire, New Mexico, Ohio, Rhode Island, and Wyoming (fig. 1; table 8). Very few wells were sampled in most of these States (table 8), so the absence of detections should be interpreted with caution. Given the widespread number and uses of VOCs in and near households throughout the United States, one or more VOCs might be detected in some domestic wells in these eight States if more sampling was done.

Detections and Geographic Distribution of VOCs by Group at an Assessment Level of 0.2 microgram per liter

Detection frequencies of VOCs by group were computed at an assessment level of 0.2 µg/L. Although VOCs frequently have multiple uses, the 55 analytes were organized into seven groups based on their primary use for purposes of comparison in this report. These groups are based on a classification developed by Bender and others (1999). Assigning an individual VOC to a use group does not imply that the designated usage is the only use for that compound. Table 6 lists the seven groups and the VOCs in each group. Most VOCs have numerous uses in industry, commerce, and households. Six of the groups include: (1) fumigants, (2) gasoline hydrocarbons, (3) compounds used for organic synthesis, (4) gasoline oxygenates, (5) refrigerants, and (6) solvents (table 9). A seventh group used in this report is the trihalomethanes (THMs). Although the title THMs does not reflect a predominant use of VOCs, THMs have been included here because they are frequently detected in ground water. For the seven groups of VOCs discussed, detection frequency is defined as the number of wells with a detection of any VOC in the group divided by the number of wells with an analysis of any VOC in the group, multiplied by 100.

Table 9. Summary of volatile organic compound detections, by group, at an assessment level of 0.2 microgram per liter

[VOCs, volatile organic compounds; >, greater than; ≤, less than or equal to]

Occurrence category	Number of VOCs	Percent of 54 VOCs	Number of VOCs in the group detected in ground water						
			Fumigants	Gasoline hydrocarbons	Organic synthesis	Gasoline oxygenates	Refrigerants	Solvents	Trihalomethanes
Compounds not detected	18	33	3	3	6	1	0	5	0
Compounds with a detection frequency >0 and <1 percent	29	54	2	3	4	2	3	12	3
Compounds with a detection frequency >1 and <5 percent	7	13	1	1	0	1	1	2	1
Total	54	100	6	7	10	4	4	19	4

By group, the 54 VOCs examined in this report include 6 fumigants, 7 gasoline hydrocarbons, 10 compounds used for organic synthesis, 4 gasoline oxygenates, 4 refrigerants, 19 solvents, and 4 THMs. All VOCs within the refrigerant and THM groups were detected; however, most of the VOCs in all of the groups (87 percent) were either not detected or detected at a frequency of equal to or less than 1 percent (table 9). Only seven VOCs (13 percent of the total number of analytes with reported concentrations) had percent detection frequencies between 1 and 5 percent. Fumigants, gasoline hydrocarbons, gasoline oxygenates, refrigerants, and THMs all had one compound with a detection frequency between 1 and 5 percent. Solvents had two VOCs with detection frequencies between 1 and 5 percent. Compounds used for organic synthesis had no VOCs with a detection frequency greater than 1 percent. The 18 VOCs with no detections (33 percent of the total number of VOCs) include 3 of the 6 fumigants; 3 of the 7 gasoline hydrocarbons; 6 of the 10 compounds used for organic synthesis; 1 of the 4 gasoline oxygenates; and 5 of the 19 solvents.

Detection frequencies of VOCs by groups ranged from 0.5 percent for VOCs used in organic synthesis to greater than 4 percent for both solvents and THMs (fig. 3). The detection frequencies of the other five use groups are less than one-half the detection frequencies of solvents and THMs. Detection frequencies of these groups, listed in decreasing order of detection, are as follows: 2.2 percent for gasoline oxygenates; 1.6 percent for refrigerants; 1.3 percent for gasoline hydrocarbons; 1.0 percent for fumigants; and 0.5 percent for compounds used for organic synthesis. Of the 1,926 samples with analyses for solvents, 89 samples (4.6 percent) contained one or more solvents. The high detection frequency for solvents could result from the large number of compounds (19) in that group and/or the common use of VOCs within the group. Sixty-three of the samples had only one solvent detected. These 63 detections included 10 different VOCs, which indicates that no single compound predominated the detection frequency of solvents.

Many of the detections within each of the groups consist of the detection of a single VOC in that group. For example, trichloromethane detected by itself comprised 77 of the 84 detections of one or more THMs. MTBE, one of the four VOCs in the gasoline oxygenate group, comprised 20 of the 30 detections (about 67 percent) of one or more gasoline oxygenates.

In addition to the detection frequency, the average half-life of each VOC group is shown in figure 3. Environmental degradation half-lives in figure 3 were obtained from Howard and others (1991) and represent the average half-life in ground water for all of VOCs in each group. With the exception of compounds used in organic synthesis, VOC groups have detection frequencies that generally are proportional to average half-lives. One reason for the discrepancy between average half-life and the detection frequency for compounds used for organic synthesis could be

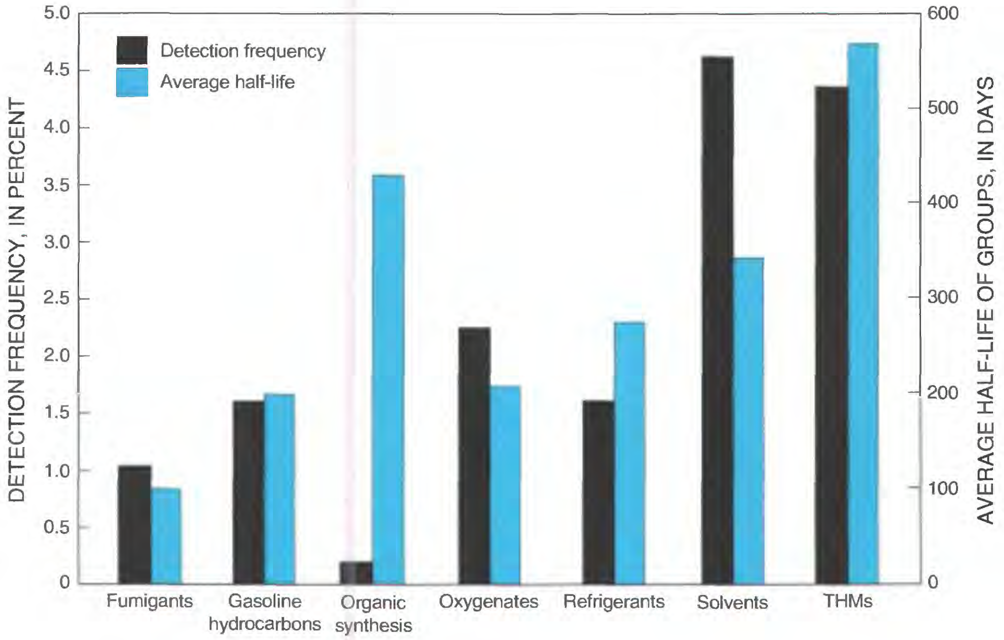


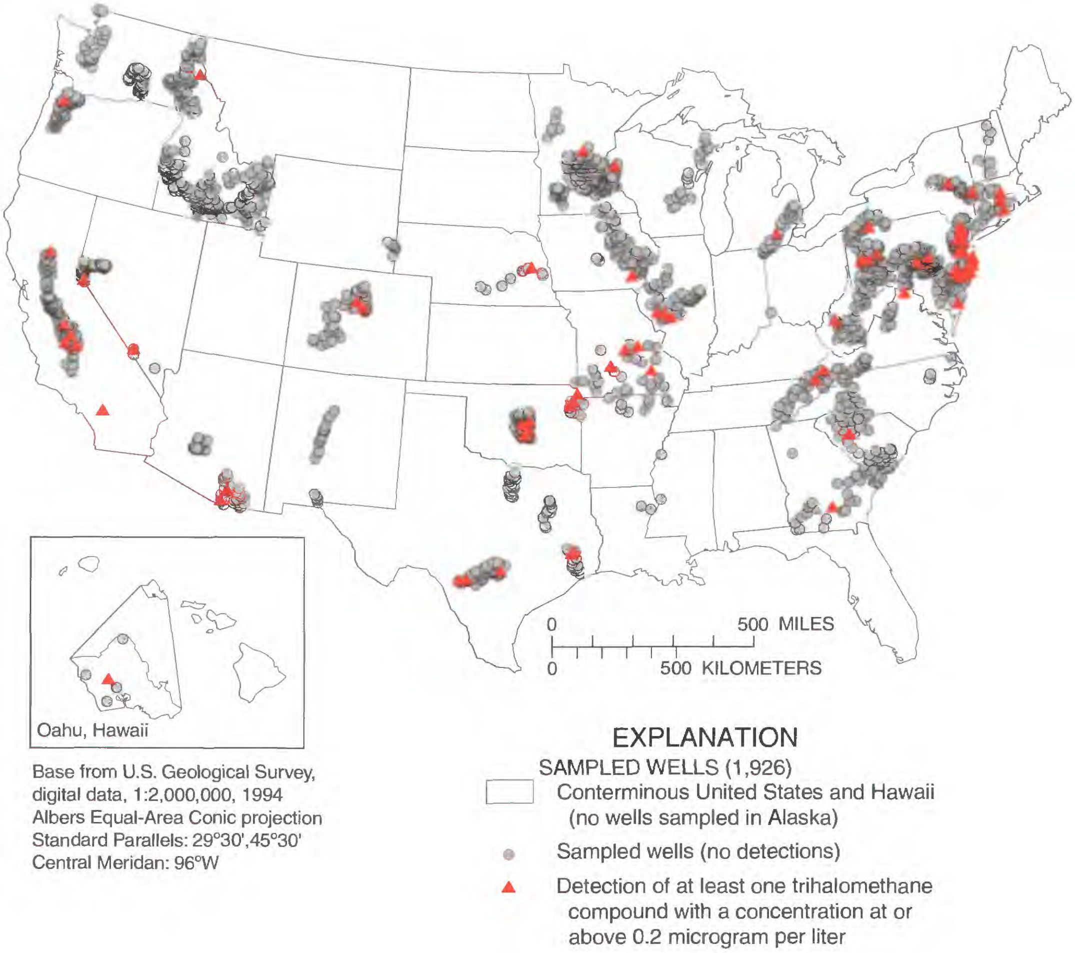
Figure 3. Detection frequency of volatile organic compound groups at an assessment level of 0.2 microgram per liter. Left side of y-axis represents frequency of detection of groups (in percent), and right side of y-axis represents the average half-life of groups (in days) (Howard and others, 1991).

minimal use of these chemicals in households. When the organic synthesis group is excluded from the analysis, there is a good correlation between the detection frequency of VOCs by group and the average half-life in days (Spearman's rho = 0.841, $p = 0.038$).

Detections of some VOC groups were widely distributed throughout the conterminous United States, whereas detections of other VOC groups were geographically concentrated in specific areas. The geographic distribution of detections of some VOC groups might relate to the use pattern of that group, whereas the distribution of detections of other VOC groups has no obvious explanation. In addition to use, factors such as climate, hydrogeology, recharge, soil and aquifer permeability, organic content of soils, ground-water redox conditions, and land use likely affect the geographic distribution of VOC groups. A more detailed review of some hydrogeologic and anthropogenic factors that could relate to VOC detections by group follows this section.

THMs had the widest geographic distribution of any of the VOC groups (fig. 4). THMs were detected in 84 domestic wells distributed throughout 27 States. Detections of solvents also had wide geographic distribution with 89 wells having detectable concentrations of solvents distributed in 20 States (fig. 5). Detections of refrigerants also had widespread distribution throughout the conterminous United States. The 31 domestic wells with detections of refrigerants were distributed throughout 18 States (fig. 6).

The 26 domestic wells with detections of gasoline hydrocarbons were fairly widely distributed throughout 15 States (fig. 7). Because of the ubiquitous use of gasoline products and widespread geographic distribution of releases to the environment, detections in ground water are expected, particularly in highly populated areas. Most of the 26 detections of gasoline hydrocarbons occurred in higher population density areas of the eastern United States and California. However, less populated States such as Arkansas, Idaho, Iowa, Minnesota, Missouri, and Texas also had detections supporting the expectation of widespread releases to the environment.



Base from U.S. Geological Survey,
digital data, 1:2,000,000, 1994
Albers Equal-Area Conic projection
Standard Parallels: 29°30',45°30'
Central Meridan: 96°W

EXPLANATION

SAMPLED WELLS (1,926)

▭ Conterminous United States and Hawaii (no wells sampled in Alaska)

● Sampled wells (no detections)

▲ Detection of at least one trihalomethane compound with a concentration at or above 0.2 microgram per liter

Figure 4. Locations where rural, untreated, self-supplied domestic well water was sampled and where at least one trihalomethane was detected.

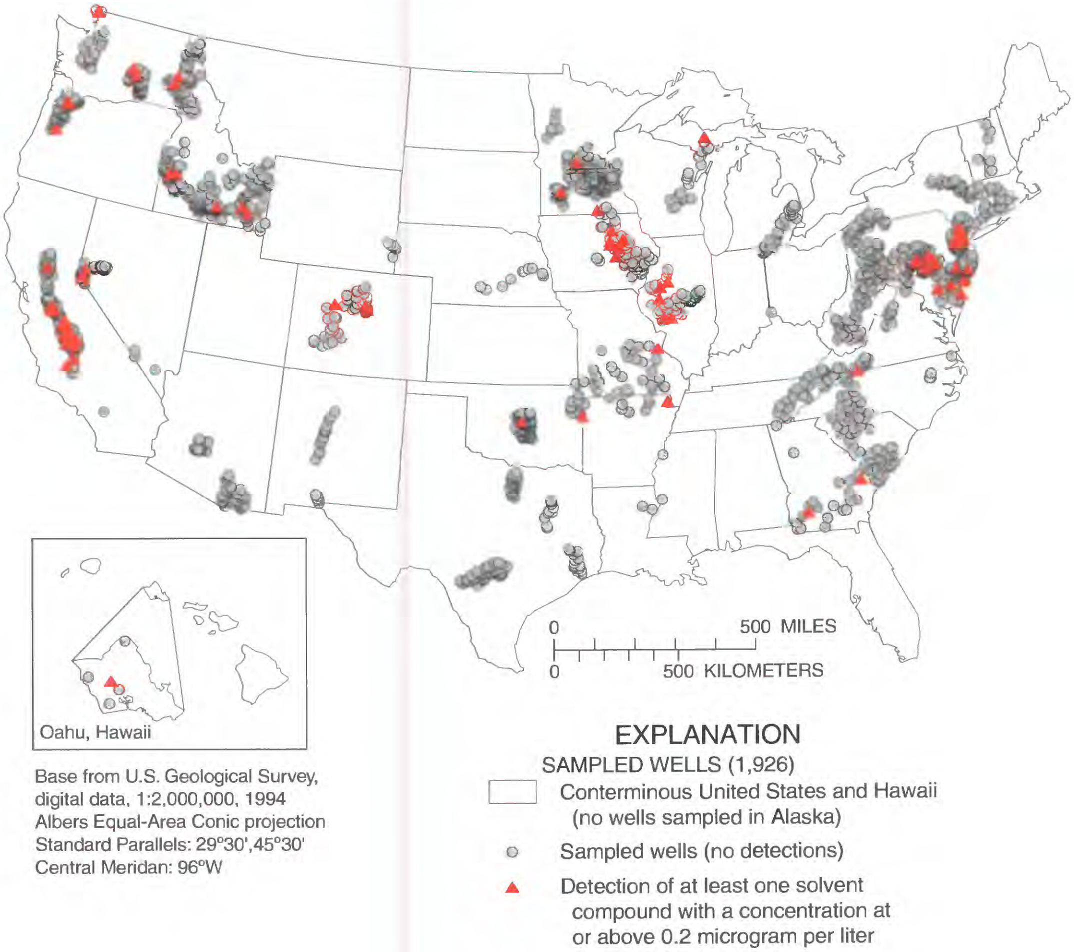
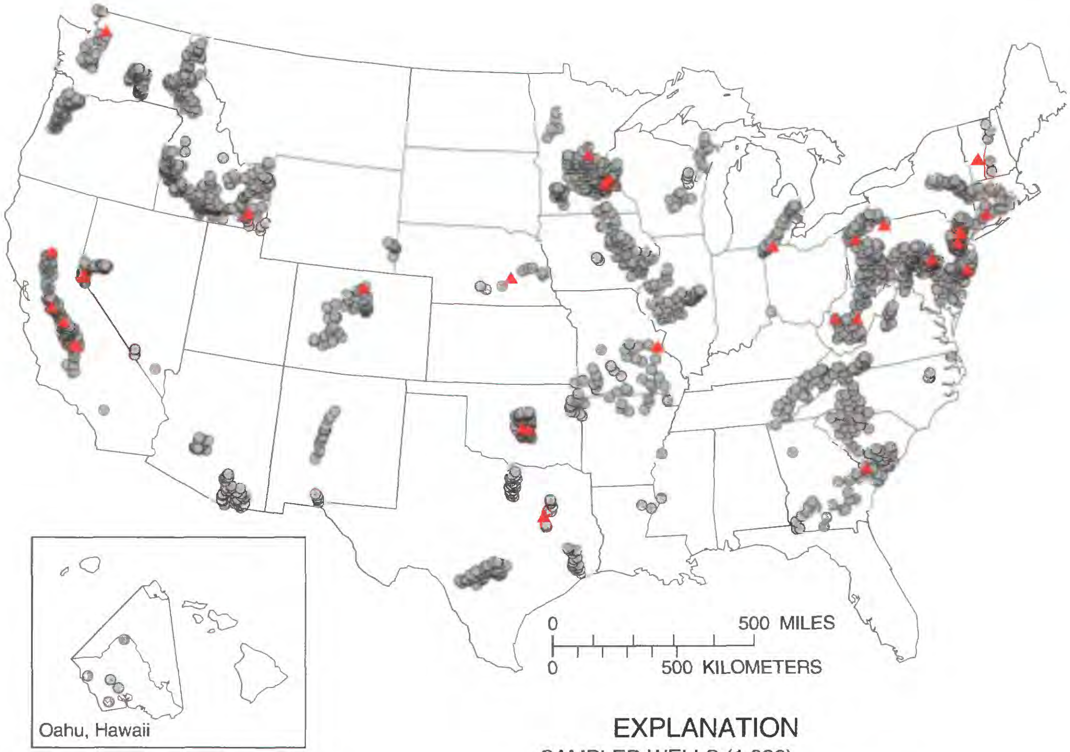


Figure 5. Locations where rural, untreated, self-supplied domestic well water was sampled and where a least one solvent was detected.



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EXPLANATION

SAMPLED WELLS (1,926)

☐ Conterminous United States and Hawaii (no wells sampled in Alaska)

● Sampled wells (no detections)

▲ Detection of at least one refrigerant compound with a concentration at or above 0.2 microgram per liter

Figure 6. Locations where rural, untreated, self-supplied domestic well water was sampled and where at least one refrigerant was detected.

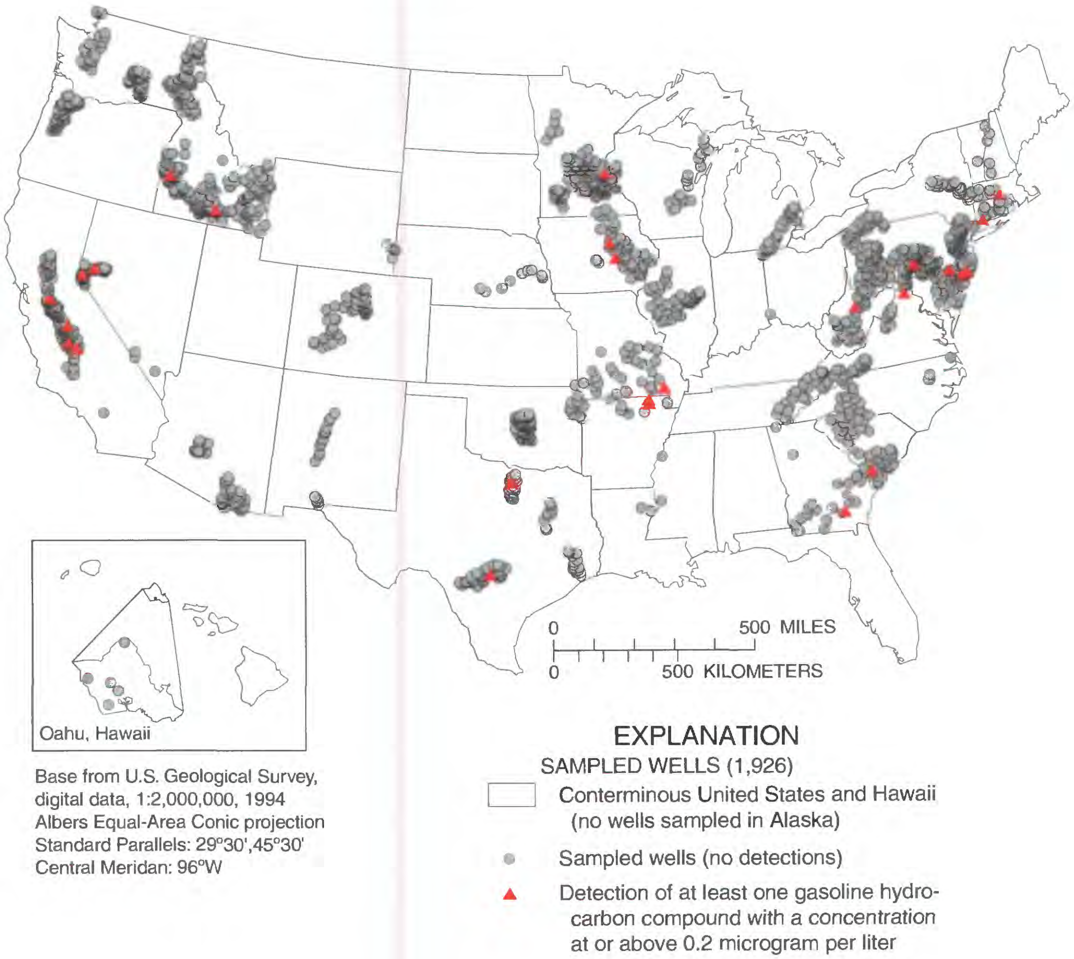


Figure 7. Locations where rural, untreated, self-supplied domestic well water was sampled and where at least one gasoline hydrocarbon was detected.

The 30 domestic wells with detections of gasoline oxygenates were distributed throughout 8 States, but detections were concentrated predominantly in the eastern portion of the United States (fig. 8A). As a result of the enactment of the Clean Air Act (CAA) Amendments of 1990 (U.S. Environmental Protection Agency, 1990b), oxygen-containing compounds 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 gasoline (OXY) program in which gasoline must contain 2.7 percent oxygen by weight during the cold season in areas that fail to meet NAAQS for carbon monoxide, and (2) the reformulated gasoline (RFG) program in which gasoline must contain 2 percent oxygen by weight year-round in areas having the highest levels of tropospheric ozone (Moran, Clawges, and Zogorski, 1999). Consequently, the use of gasoline oxygenates is concentrated in the OXY and RFG program areas. Locations of both former and current OXY and RFG areas are shown in figure 8B.

The four compounds in the gasoline oxygenate group are *tert*-amyl methyl ether, diisopropyl ether, ethyl *tert*-butyl ether, and MTBE. Any of these can be used in gasoline as an oxygenate, but MTBE is used most frequently. The first cold season oxygenated gasoline program in the United States was voluntarily implemented in Denver, Colorado, in 1988 (Office of Science and Technology, 1997). One oxygenate was detected in a domestic well within this area (fig. 8B). Detections of oxygenates occurred in 5 of the 18 States with large areas that have participated, or presently are participating in the OXY and RFG programs. These include 12 detections in New Jersey, 6 detections in Pennsylvania, 3 detections in Connecticut, 2 detections in Massachusetts, and 1 detection in Illinois (fig. 8B). Although MTBE is used throughout California in the State's reformulated gasoline program, no oxygenates were detected in domestic wells sampled there. One reason for the lack of oxygenate detections in California may be that all of the domestic wells sampled are located in the Central Valley where land use is predominantly agricultural. Ground water under areas of agricultural land use would be expected to have a lower overall usage of gasoline compared to other areas and thus have a smaller number of potential sources.

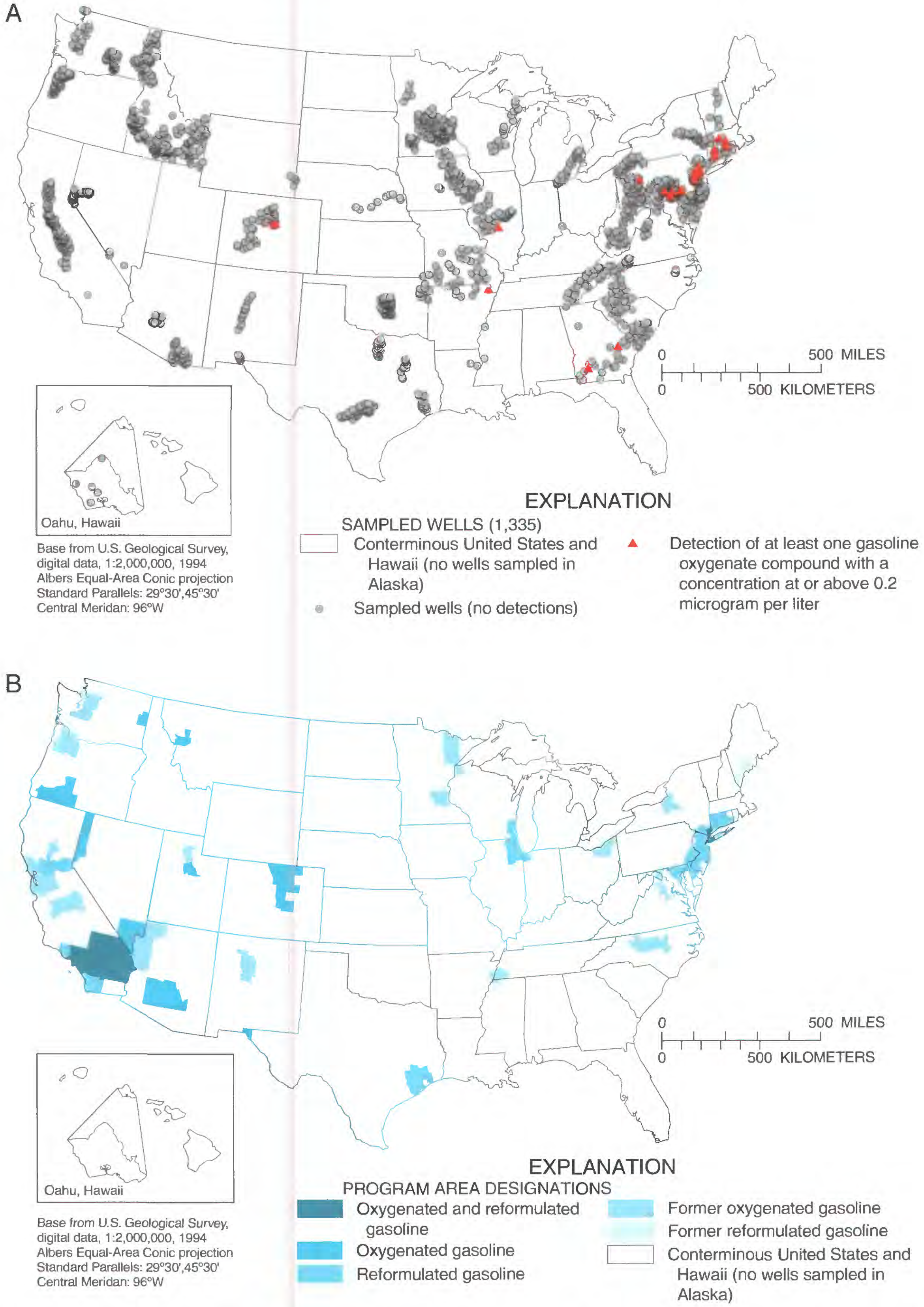
Compounds used in organic synthesis were geographically restricted with detections in only nine domestic wells in six States (fig. 9). Minimal detections of these VOCs in rural domestic wells would be expected because they are predominantly used as intermediates for production of other compounds and, as such, would most likely be associated with industrial settings and would not be expected to have many sources near domestic wells.

Of all the VOC groups, fumigants had the most restricted geographic distribution with detections in 20 domestic wells in only three States (fig. 10). Sixteen of these detections (80 percent) occurred in the Central Valley of California. Because fumigants are used for insect and nematode control in vineyards and orchards, detections in agricultural areas with emphasis on these types of crops, such as the Central Valley of California, would be expected. Washington and New Jersey had two wells each with detections of VOCs in the fumigant group.

Detections of Individual VOCs at an Assessment Level of 0.2 microgram per liter

Detection frequencies for individual VOCs were computed at an assessment level of 0.2 µg/L. Fifty-five VOCs are targeted by NAWQA (table 4), but the concentrations of 1,3-dimethylbenzene and 1,4-dimethylbenzene cannot be separated by the NWQL and are reported together. Therefore, results for only 54 individual analytes are presented here. Occurrence information presented for each VOC includes the number of detections of the VOC, the number of samples in which the VOC was analyzed, the detection frequency, VOC concentrations, and ranges in concentration.

VOC detections are organized into three groups in table 10: (1) VOCs not detected in any samples; (2) VOCs detected at a frequency of less than or equal to 1 percent; and (3) VOCs detected at a frequency of greater than 1 percent and less than 5 percent. No individual VOC had a detection frequency greater than 5 percent. Of the 54 VOCs, 18 (33 percent) were not detected, 29 (54 percent) had detection frequencies of less than or equal to 1 percent, and 7 (13 percent) had detection frequencies of greater than 1 percent and less than 5 percent. The most frequently detected individual VOC was trichloromethane with a detection frequency of 4.3 percent (fig. 11). The detections of individual VOCs are summarized in table 11. Figure 11 illustrates the detection frequency of individual VOCs.



Base from U.S. Geological Survey,
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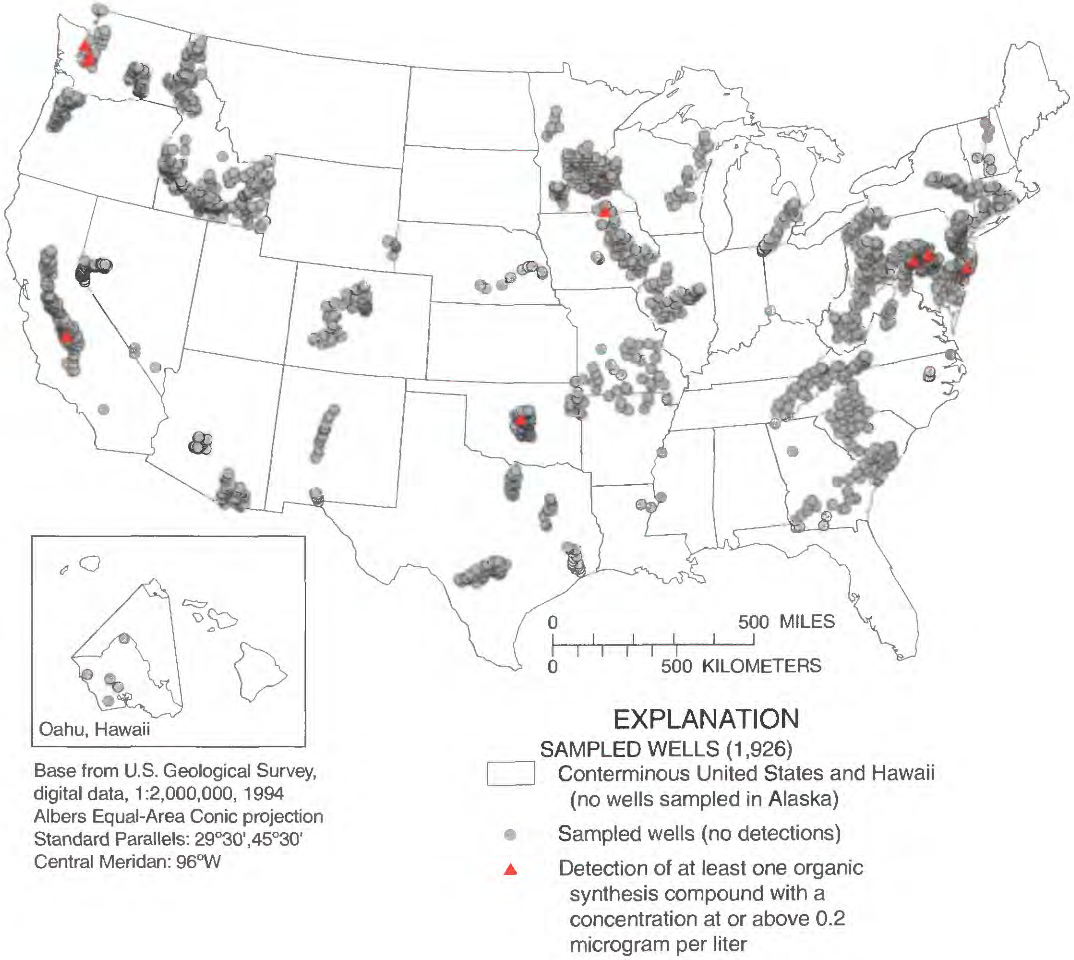
Figure 8. Locations (A) where rural, untreated, self-supplied domestic well water was sampled and where at least one gasoline oxygenate was detected and (B) of Federal oxygenated and reformulated gasoline program areas and locations.



Base from U.S. Geological Survey,
digital data, 1:2,000,000, 1994
Albers Equal-Area Conic projection
Standard Parallels: 29°30',45°30'
Central Meridan: 96°W

Figure 9. Locations where rural, untreated, self-supplied domestic well water was sampled and where at least one volatile organic compound used for organic synthesis was detected.

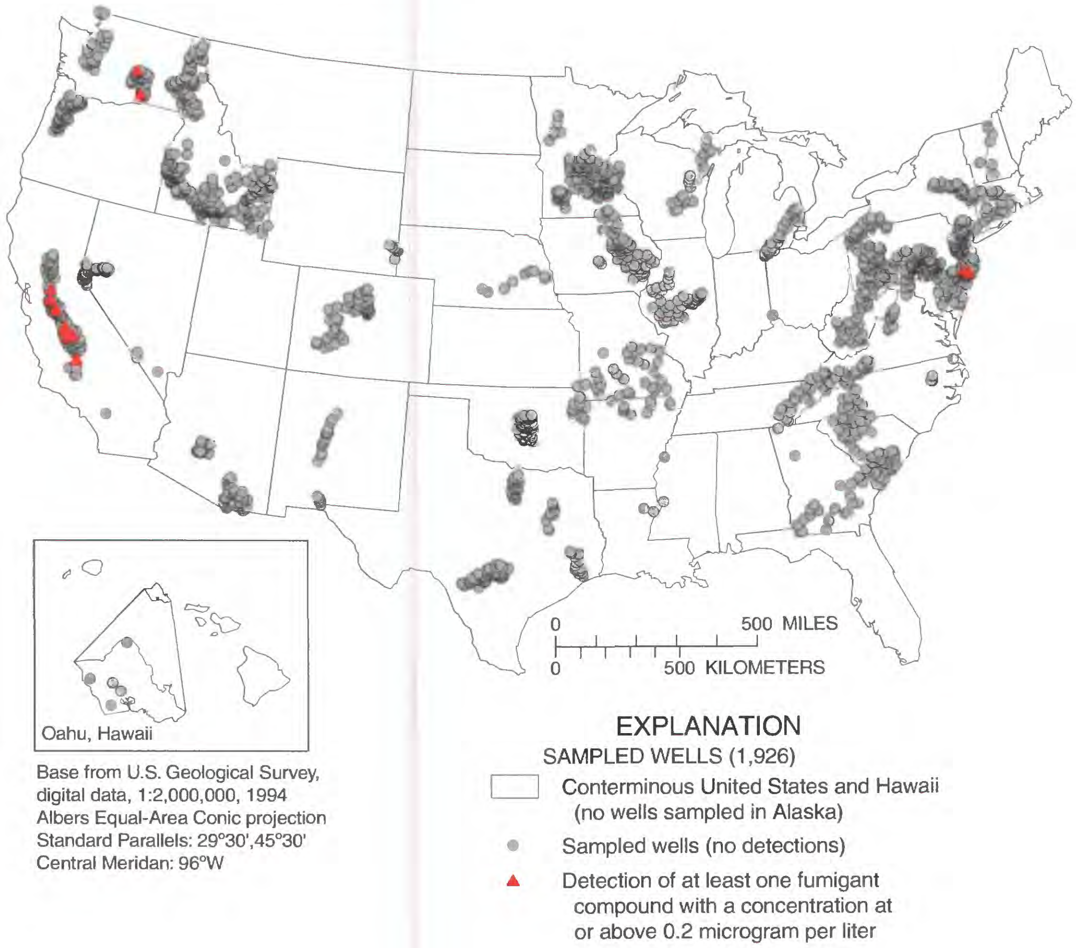


Figure 10. Locations where rural, untreated, self-supplied domestic well water was sampled and where at least one fumigant was detected.

Table 10. Detections of individual volatile organic compounds at an assessment level of 0.2 microgram per liter

[VOC, volatile organic compound; Min., minimum; Max., maximum; MCL, Maximum Contaminant Level; HA, Health-Advisory Level, lifetime 70-kilogram adult consuming 2 liters of water per day; 10^{-4} CR, risk of one additional 70-kilogram adult in ten thousand (1×10^{-4}) contracting cancer over a lifetime of exposure consuming 2 liters of water per day; µg/L, micrograms per liter; --, not applicable]

Volatile organic compound	Predominant use	Number of detections/ samples	Detected concentrations (in µg/L)			Type of drinking-water standard, health criterion, or taste/odor threshold			
			Min	Median	Max	MCL, HA, 10^{-4} CR (µg/L)	Number of concentrations exceeding standard or criterion	Taste/odor threshold[1] (µg/L)	Number of concentrations exceeding taste/odor threshold
				VOCs Not Detected					
Bromomethane	Fumigant	0/1,677	--	--	--	10 (HA)	0	--	0
cis-1,3-Dichloropropene	Fumigant	0/1,685	--	--	--	40 (10^{-4} CR)	0	--	0
trans-1,3-Dichloropropene	Fumigant	0/1,592	--	--	--	40 (10^{-4} CR)	0	--	0
n-Butylbenzene	Gasoline hydrocarbon	0/1,454	--	--	--	--	0	--	0
1,2-Dimethylbenzene	Gasoline hydrocarbon	0/805	--	--	--	10,000 (MCL)	0	--	0
1,3/1,4-Dimethylbenzene	Gasoline hydrocarbon	0/799	--	--	--	10,000 (MCL)	0	[2]17	0
Bromoethene	Organic synthesis	0/688	--	--	--	--	0	--	0
Hexachlorobutadiene	Organic synthesis	0/1,347	--	--	--	1 (HA)	0	6	0
2-Propenal	Organic synthesis	0/472	--	--	--	--	0	110	0
2-Propenenitrile	Organic synthesis	[3]0/693	--	--	--	6 (10^{-4} CR)	0	9,100	0
Ethenylbenzene	Organic synthesis	0/1,915	--	--	--	100 (MCL and HA)	0	11	0
1,2,3-Trichlorobenzene	Organic synthesis	0/1,455	--	--	--	--	0	10	0
Ethyl *tert*-butyl ether	Oxygenate	0/688	--	--	--	--	0	--	0
1,2-Dichlorobenzene	Solvent	0/1,911	--	--	--	600 (MCL)	0	24	0
1,3-Dichlorobenzene	Solvent	0/1,340	--	--	--	600 (HA)	0	77	0
Hexachloroethane	Solvent	0/698	--	--	--	1 (HA)	0	10	0
1,2,4-Trichlorobenzene	Solvent	0/1,464	--	--	--	70 (MCL)	0	5	0
1,1,2-Trichloroethane	Solvent	0/1,686	--	--	--	5 (MCL)	0	50,000	0

Table 10. Detections of individual volatile organic compounds at an assessment level of 0.2 microgram per liter–Continued

[VOC, volatile organic compound; Min., minimum; Max., maximum; MCL, Maximum Contaminant Level; HA, Health-Advisory Level, lifetime 70-kilogram adult consuming 2 liters of water per day; 10^{-4} CR, risk of one additional 70-kilogram adult in ten thousand (1×10^{-4}) contracting cancer over a lifetime of exposure consuming 2 liters of water per day; µg/L, micrograms per liter; --, not applicable]

Volatile organic compound	Predominant use	Number of detections/ samples	Detected concentrations (in µg/L)			Type of drinking-water standard, health criterion, or taste/odor threshold			
			Min	Median	Max	MCL, HA, 10^{-4} CR (µg/L)	Number of concentrations exceeding standard or criterion	Taste/odor threshold[1] (µg/L)	Number of concentrations exceeding taste/odor threshold
Detection Frequency Greater Than 0 and Less Than or Equal to 1 Percent									
1,2-Dibromoethane	Fumigant	[3]3/1,614	0.3	0.6	1.1	0.05 (MCL)	3	--	--
1,4-Dichlorobenzene	Fumigant	1/1,925	1.2	1.2	1.2	75 (MCL)	0	4.5	0
Benzene	Gasoline hydrocarbon	6/1,892	0.2	0.5	4.4	5 (MCL)	0	170	0
Ethylbenzene	Gasoline hydrocarbon	2/1,926	0.2	2.8	5.4	700 (MCL)	0	29	0
Naphthalene	Gasoline hydrocarbon	2/1,464	1.8	2.1	2.5	20 (HA)	0	2.5	0
1,2,4-Trimethylbenzene	Gasoline hydrocarbon	6/1,415	0.2	0.3	12	--	-	500	0
Chloroethene	Organic synthesis	1/1,917	0.4	0.4	0.4	2 (MCL)	0	3,400	0
1,1-Dichloroethene	Organic synthesis	2/1,926	0.5	19.8	39	7 (MCL)	1	1,500	0
(1-Methylethyl) benzene	Organic synthesis	2/1,371	0.4	0.6	0.8	233 (10^{-4} CR)	0	0.8	0
tert-Amyl methyl ether	Oxygenate	1/688	0.8	0.8	0.8	--	--	--	--
Diisopropyl ether	Oxygenate	1/581	22	22	22	--	--	--	--
Chloromethane	Refrigerant	2/1,565	1.1	1.8	2.5	3 (HA)	0	--	--
Trichlorofluoromethane	Refrigerant	7/1,925	0.2	0.3	1.9	2,000 (HA)	0	28	0
1,1,2-Trichloro-1,2,2-trifluoroethane	Refrigerant	1/1,515	0.3	0.3	0.3	2,100,000 (10^{-4} CR)	0	--	--
Chlorobenzene	Solvent	1/1,926	3.5	3.5	3.5	100 (MCL)	0	50	0
Chloroethane	Solvent	2/1,677	0.3	0.5	0.7	--	--	19	0
1,1-Dichloroethane	Solvent	5/1,926	0.2	0.7	1.7	--	--	--	--
1,2-Dichloroethane	Solvent	4/1,910	0.2	1.5	2.9	5 (MCL)	0	7,000	0
cis-1,2-Dichloroethene	Solvent	2/1,705	3	3.7	4.4	70 (MCL)	0	--	--
trans-1,2-Dichloroethene	Solvent	1/1,767	0.4	0.4	0.4	100 (MCL)	0	4.3	0

Table 10. Detections of individual volatile organic compounds at an assessment level of 0.2 microgram per liter–Continued

[VOC, volatile organic compound; Min., minimum; Max., maximum; MCL, Maximum Contaminant Level; HA, Health-Advisory Level, lifetime 70-kilogram adult consuming 2 liters of water per day; 10^{-4} CR, risk of one additional 70-kilogram adult in ten thousand (1 x 10^{-4}) contracting cancer over a lifetime of exposure consuming 2 liters of water per day; µg/L, micrograms per liter; --, not applicable]

Volatile organic compound	Predominant use	Number of detections/ samples	Detected concentrations (in µg/L)			Type of drinking-water standard, health criterion, or taste/odor threshold			
			Min	Median	Max	MCL, HA, 10^{-4} CR (µg/L)	Number of concentrations exceeding standard or criterion	Taste/odor threshold[1] (µg/L)	Number of concentrations exceeding taste/odor threshold
Detection Frequency Greater Than 0 and Less Than or Equal to 1 Percent—Continued									
Dichloromethane	Solvent	12/1,923	0.2	0.6	4	5 (MCL)	0	910	0
1,2-Dichloropropane	Solvent	15/1,926	0.2	0.5	19.4	5 (MCL)	2	10	1
n-Propylbenzene	Solvent	1/1,454	0.6	0.6	0.6	--	--	--	--
Tetrachloromethane	Solvent	5/1,925	0.2	0.4	0.6	5 (MCL)	0	520	0
Trichloroethene	Solvent	16/1,926	0.2	0.7	25	5 (MCL)	3	310	0
1,2,3-Trichloropropane	Solvent	10/1,615	0.2	0.4	2.1	40 (HA)	0	--	--
Bromodichloromethane[4]	Trihalomethane	7/1,926	0.2	1.5	7	80 (MCL)	0	--	--
Chlorodibromomethane[4]	Trihalomethane	7/1,926	0.3	0.6	11	80 (MCL)	0	--	--
Tribromomethane[4]	Trihalomethane	4/1,925	0.3	0.7	8.2	80 (MCL)	0	300	0
Detection Frequency Greater Than 1 and Less Than or Equal to 5 Percent									
1,2-Dibromo-3-chloropropane	Fumigant	[5]16/1,459	0.2	1.3	3.2	0.2 (MCL)	16	--	--
Methylbenzene	Gasoline hydrocarbon	21/1,882	0.2	0.3	12	1,000 (MCL)	0	42	0
Methyl *tert*-butyl ether	Oxygenate	30/1,335	0.2	0.7	30.2	--	--	[6]20	1
Dichlorodifluoromethane	Refrigerant	23/1,916	0.2	0.3	2	1,000 (HA)	0	--	--
Tetrachloroethene	Solvent	32/1,897	0.2	0.3	29	5 (MCL)	3	190	0
1,1,1-Trichloroethane	Solvent	22/1,926	0.2	0.4	120	200 (MCL)	0	970	0
Trichloromethane[4]	Trihalomethane	83/1,926	0.2	0.5	74	80 (MCL)	0	2,400	0

[1] Taste/odor thresholds from Bender and others, 1999.

[2] 1,3-Dimethylbenzene.

[3] No additional detections exist below 0.2 µg/L.

[4] Bromodichloromethane, chlorodibromomethane, tribromomethane, and trichloromethane can also be classified as solvents or VOCs used in organic synthesis.

[5] When uncensored, the number of detections equals 19.

[6] Lower limit of U.S. Environmental Protection Agency Drinking Water Advisory.

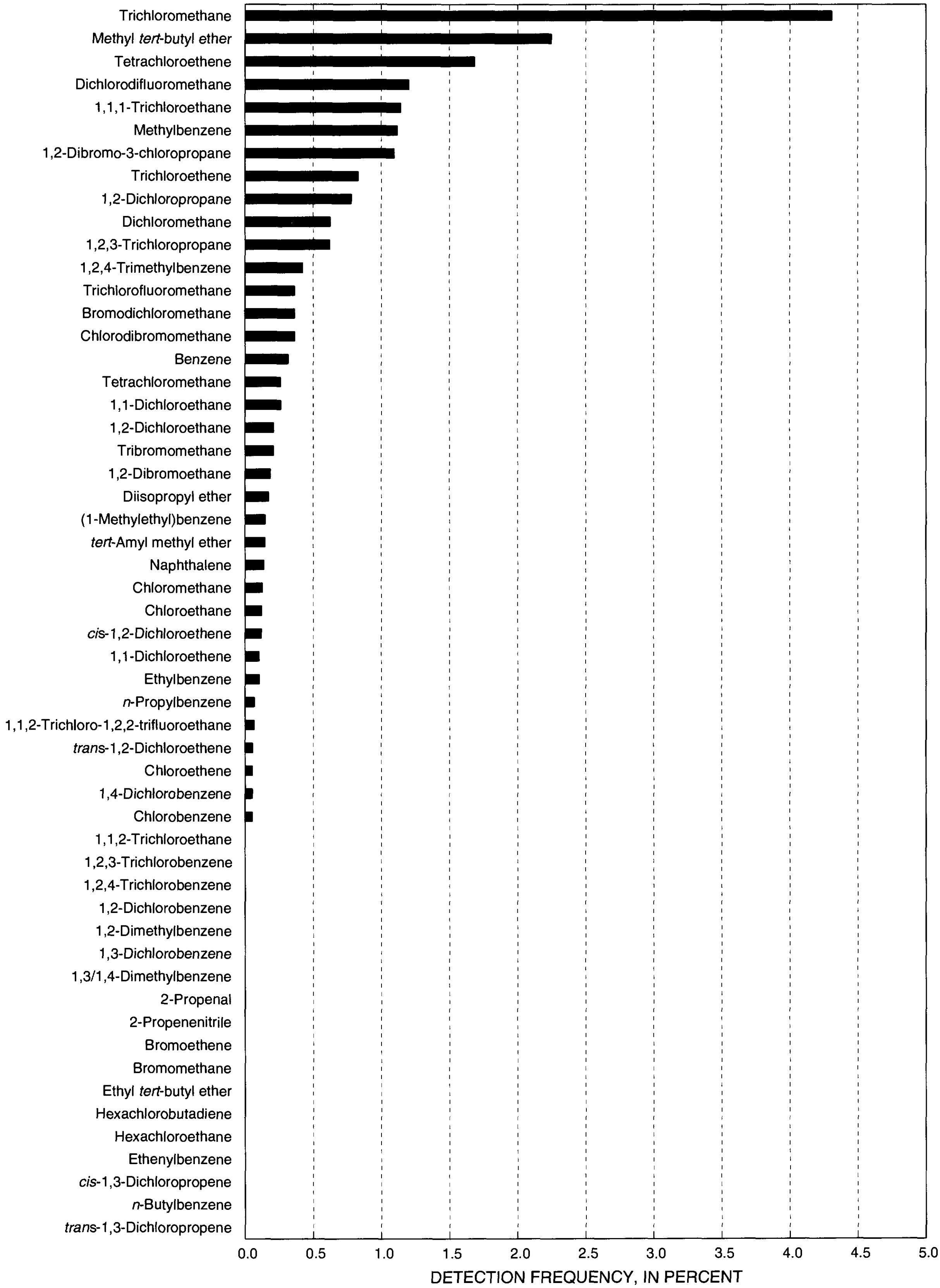


Figure 11. Detection frequencies of 54 volatile organic compounds at an assessment level of 0.2 microgram per liter.

Table 11. Summary of detections of individual volatile organic compounds at an assessment level of 0.2 microgram per liter

[VOC, volatile organic compound; >, greater than; ≤, less than or equal to]

Occurrence category	Number of VOCs	Percent of 54 VOCs	Occurrences exceeding a drinking-water standard, health criterion, or taste/odor threshold
VOCs not detected	18	33	0
VOCs with a detection frequency >0 and ≤1 percent	29	54	10
VOCs with a detection frequency >1 and ≤5 percent	7	13	20
VOCs with a detection frequency >5 percent	0	0	0
Total	54	100	30

The VOCs listed in table 10 have a variety of uses. The 18 VOCs that were not detected and the 29 VOCs with detection frequencies less than 1 percent represent six predominant uses. The seven VOCs that had the highest detection frequencies included: trichloromethane, MTBE, tetrachloroethene, dichlorodifluoromethane, 1,1,1-trichloroethane, methylbenzene, and 1,2-dibromo-3-chloropropane. These VOCs represent all uses except organic synthesis. Detection or detection frequency of a VOC does not appear to be related to its use as indicated by the lack of clustering of VOCs in certain use groups by detection frequency.

Status of VOC Concentrations

Table 10 gives ranges of concentrations for every VOC that was detected. Status information includes exceedances of VOCs relative to various drinking-water standards (MCLs), health criteria (HA), and taste/odor thresholds. All concentration data for individual VOCs are considered at or above a concentration of 0.2 µg/L.

Under the SDWA, the USEPA has established legally enforceable water-quality standards, or MCLs, for CWSs and NTNCWSs based on overall health risks (U.S. Environmental Protection Agency, 1999a). The MCL is the highest level of a contaminant that is allowed in drinking water and is set as close to the Maximum Contaminant Level Goals (MCLG) as is feasible based upon treatment technologies, costs, and other factors (U.S. Environmental Protection Agency, 2000a). The USEPA also has established health criteria that are not legally enforceable such as Lifetime Health Advisories (HA) and excess lifetime cancer risks that are believed to be protective of carcinogenic and noncarcinogenic human health effects. In this report, health criteria refer to either HAs or excess lifetime cancer risks. Drinking-Water Advisories (DWA) and taste/odor thresholds, which are not legally enforceable, also have been recommended by the USEPA to address acceptable drinking-water concentrations for a chemical substance based on cosmetic effects such as tooth or skin discoloration or aesthetic effects such as taste, odor, and color (U.S. Environmental Protection Agency, 2000a). Values for MCLs, health criteria, and taste/odor thresholds were taken from Bender and others (1999).

Forty-two of the 54 VOCs have drinking-water standards or health criteria (table 10). Thirty-seven of the target VOCs have either MCLs, HAs, or both (1,3-dimethylbenzene and 1,4-dimethylbenzene are reported together), and 14 have only HAs or excess lifetime cancer risks. Thirty-three VOCs have either a DWA or taste/odor threshold.

The concentrations of VOCs relative to drinking-water standards, health criteria, or taste/odor thresholds were examined in two ways: (1) the number of samples with one or more VOCs exceeding a drinking-water standard, health criterion, or taste/odor threshold, and (2) the total number of times that an individual VOC exceeded a drinking-water standard, health criterion, or taste/odor threshold. If a VOC did not have an MCL but had both an HA and an excess lifetime cancer risk, the lowest value of either was taken for comparison to VOC concentrations. The excess lifetime cancer risk was examined at 10^{-4} level.

Figure 12 illustrates the detected concentrations of all VOCs. Most concentrations were relatively low. Maximum concentrations of most VOCs detected were less than 10 µg/L, but 11 of the 54 VOCs had at least one detection with a concentration greater than 10 µg/L (table 10; fig. 12). Seven of these 11 VOCs had at least one detection with a concentration that exceeded 20 µg/L. Trichloromethane and 1,1,1-trichloroethane had at least one detection with a concentration that exceeded 50 µg/L.

Twenty-seven samples (1.4 percent) had at least one VOC that exceeded either an MCL, a health criterion, or both. Two samples (0.1 percent) had at least one VOC that exceeded a DWA or taste/odor threshold.

Only six VOCs exceeded either an MCL or health criterion in a total of 28 occurrences. The six VOCs that exceeded an MCL at least once were 1,2-dibromoethane, 1,1-dichloroethene, 1,2-dichloropropane, trichloroethene, 1,2-dibromo-3-chloropropane, and tetrachloroethene. Sixteen of the 28 exceedances of an MCL (57 percent) were by one compound, 1,2-dibromo-3-chloropropane (DBCP). The MCL for DBCP is relatively low (0.2 µg/L) compared to MCLs for other VOCs (table 10). Of the 16 exceedances of DBCP, 15 occurred in the Central Valley of California and one occurred in New Jersey. The exceedances in California are logical because DBCP was used extensively in vineyards and orchards as a soil fumigant for insects and nematodes prior to its ban in 1985, and these types of agricultural areas are common in the Central Valley of California (U.S. Environmental Protection Agency, 2001). Trichloroethene, tetrachloroethene, and 1,2-dibromoethane exceeded their MCLs in three occurrences each. Trichloroethene and tetrachloroethene are both commonly used solvents and 1,2-dibromoethane is another commonly used fumigant. Only two VOCs exceeded a DWA or taste/odor threshold, each only once. The two VOCs that exceeded a DWA or taste/threshold were 1,2-dichloropropane and MTBE (table 10).

Detections of VOCs Using No Assessment Level

Previous occurrence results have been reported at an assessment level of 0.2 µg/L. Most VOCs analyzed by NAWQA since April 1996 have variable laboratory reporting levels that can differ between individual VOCs by as much as an order of magnitude and also can vary over time for an individual VOC (Oblinger Childress and others, 1999).

To fully understand the effect that differing laboratory reporting levels have on water-quality information, the detection frequency of one or more VOC versus assessment level should be examined. Figure 13 illustrates how detection frequency of one or more VOCs varies with assessment level for the data set used in this study. In this instance, the assessment level is used to illustrate the effect that varying laboratory reporting levels can have on detection frequency.

As assessment level is increased, the detection frequency decreases (fig. 13). Individual VOCs, or subsets of VOCs, that have different laboratory reporting levels, like the differing assessment levels shown in figure 13, can have different detection frequencies. Comparisons of detection frequencies between groups of VOCs or between individual VOCs that have variable laboratory reporting levels, without applying an assessment level, may not reflect true differences in water quality. Rather than demonstrating differences in water quality, differences in detection frequencies between analytes or VOC subsets with different reporting levels may simply show differences in resolving power of the analytical instrument with respect to various compounds or differences in laboratory reporting levels between various laboratories if the data are from various sources.

Applying an assessment level can improve comparisons between analytes or VOC subsets with different reporting levels by subjecting both to an equal level of assessment. However, applying an assessment level can cause a loss of important information. For those VOCs with many analyses at a laboratory reporting level lower than the chosen assessment level, a great deal of information on occurrence of that VOC may be lost. The frequency of detection of a particular VOC might be underestimated (biased low) when the assessment level is significantly higher than the laboratory reporting level. Therefore, it is important to understand the effect of assessment level on the frequency of detection of individual VOCs.

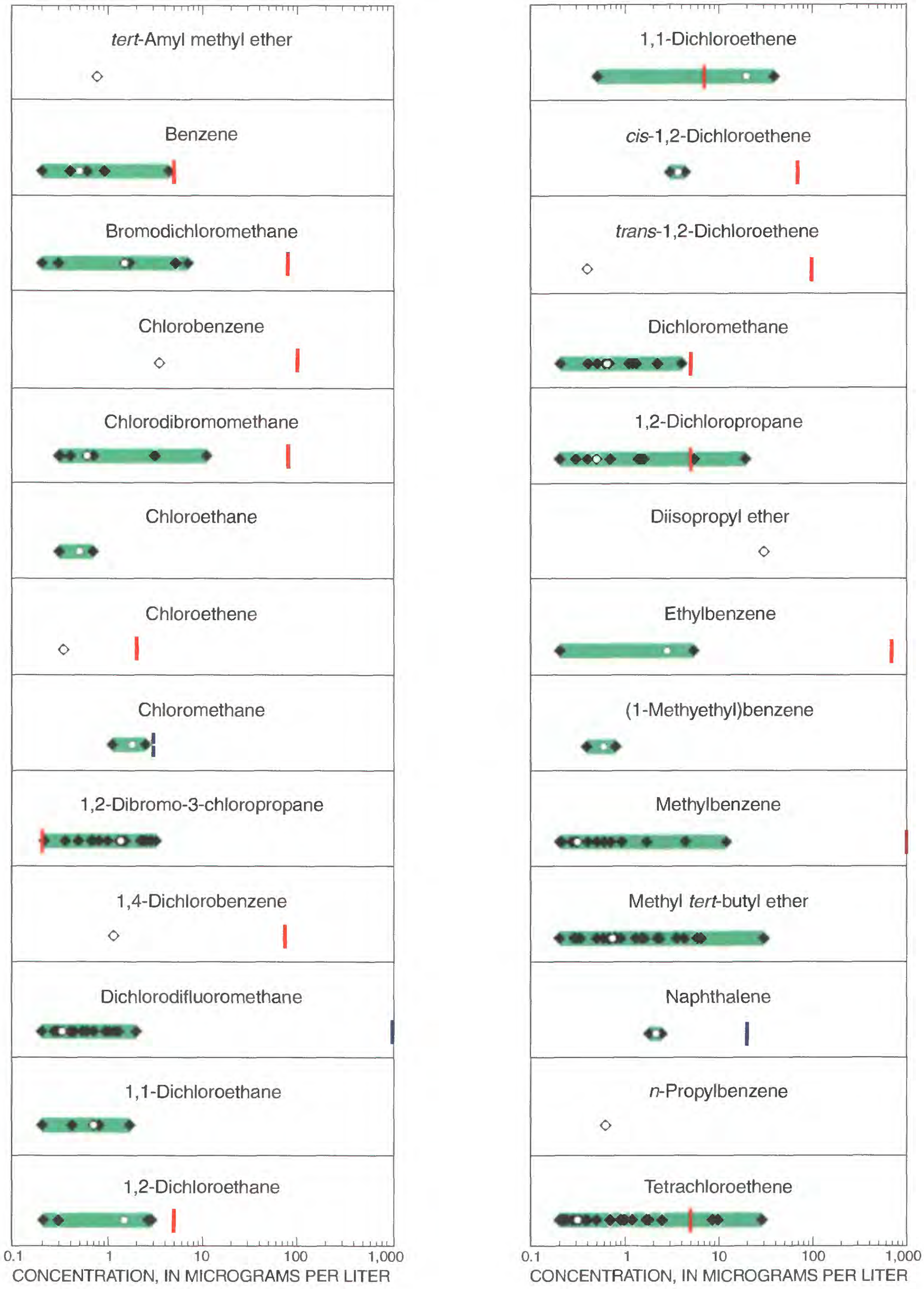


Figure 12. Concentrations of volatile organic compounds detected at an assessment level of 0.2 micrograms per liter.

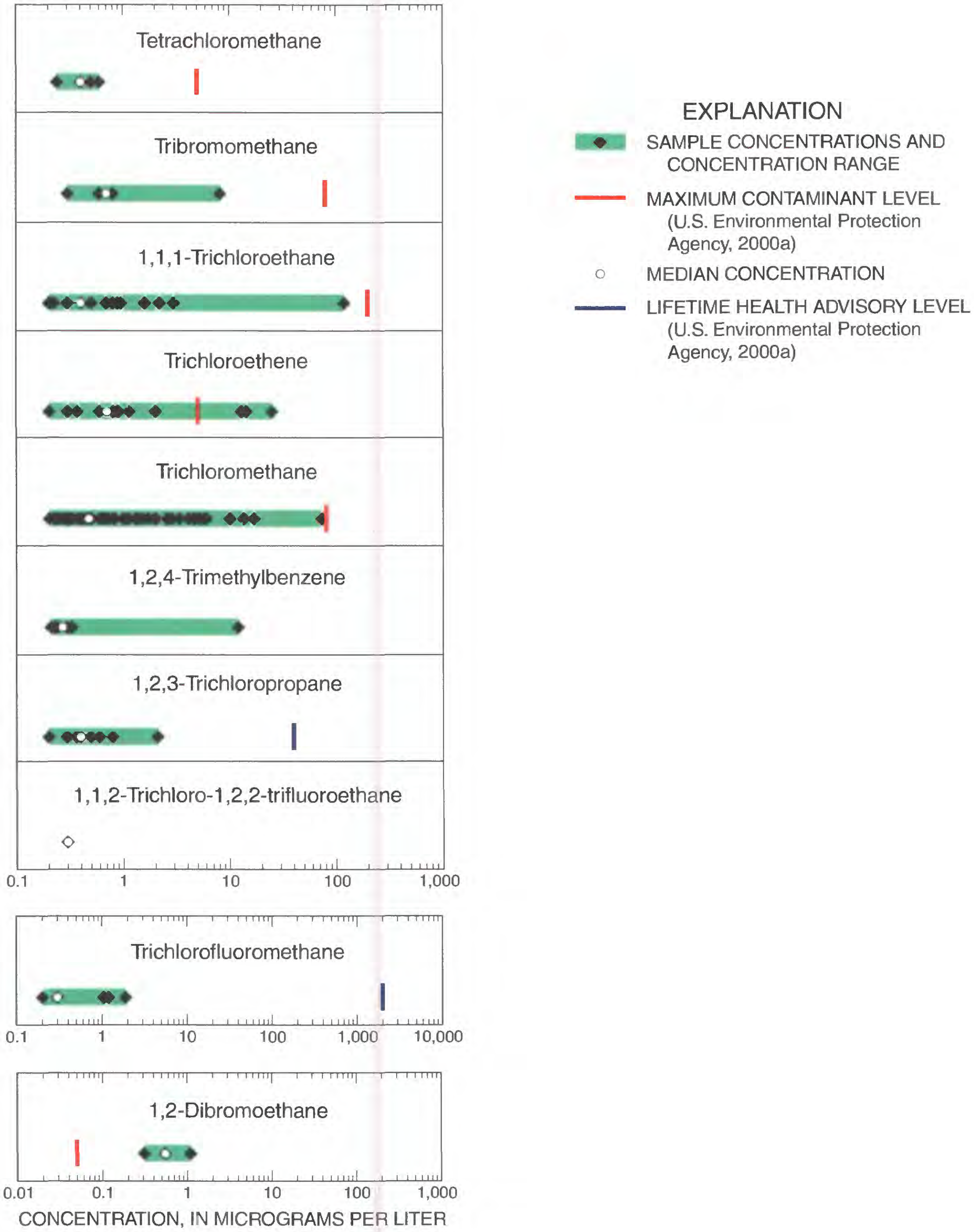


Figure 12. Concentrations of volatile organic compounds detected at an assessment level of 0.2 micrograms per liter.—Continued

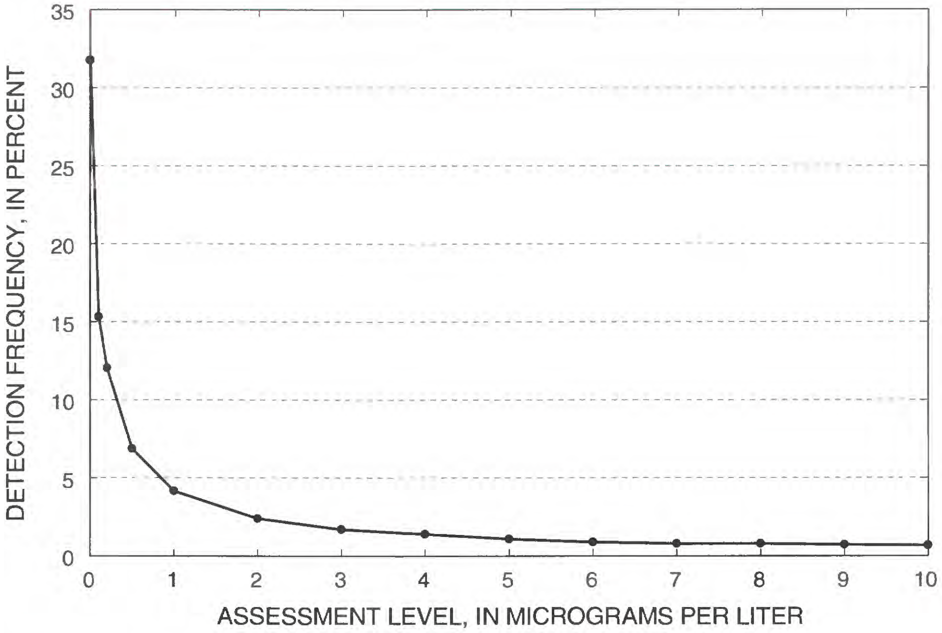


Figure 13. Detection frequency of one or more volatile organic compounds versus assessment level for samples from this study.

The data in table 12 illustrate the change in detection frequency that can occur as a result of applying various assessment levels. Detection frequencies of 54 VOCs were calculated after censoring the data at three different assessment levels: (1) no assessment level; (2) 0.05 µg/L; and (3) 0.2 µg/L. Most compounds were detected at one or more assessment levels, but 12 VOCs were not detected at any assessment level including 2-propenal, 2-propenenitrile, hexachloroethane, bromomethane, 1,1,2-trichloroethane, 1,2,4-trichlorobenzene, *trans*-1,3-dichloropropene, *cis*-1,3-dichloropropene, hexachlorobutadiene, bromoethene, ethyl *tert*-butyl ether, and 1,2,3-trichlorobenzene. The implications of the lack of detections of these compounds are that these compounds are not ground-water contaminants in the areas that were sampled, or that these compounds are present in ground water in the areas sampled but at concentrations less than the laboratory's analytical capability.

Five compounds were not detected at an assessment level of 0.2 µg/L but were detected at an assessment level of 0.05 µg/L and at no assessment level: 1,3-dimethylbenzene/1,4-dimethylbenzene, 1,2-dimethylbenzene, ethenylbenzene, 1,3-dichlorobenzene, and 1,2-dichlorobenzene. One compound, *n*-butylbenzene, was not detected at assessment levels of 0.2 or 0.05 µg/L, but was detected at no assessment level. Most compounds that were detected at all three assessment levels were detected more frequently at lower or no assessment levels.

VOCs show variations in detection frequencies with differing assessment levels. A good way to examine this variability is with a ratio of detection frequencies. The ratio of detection frequency of an individual VOC at one assessment level divided by its detection frequency at another assessment level is the detection-frequency ratio. A detection-frequency ratio was computed for detection at no assessment level versus detection at an assessment level of 0.2 µg/L (table 12). The median detection-frequency ratio for all VOCs is 2.3, and most compounds that were detected have detection-frequency ratios less than 5 (table 12). Several VOCs have substantially higher detection-frequency ratios than other compounds. Chloromethane and 1,2,4-trimethylbenzene, in particular, have detection-frequency ratios (73 and 24, respectively) that are substantially greater than the other 52 VOCs. The high detection-frequency ratios for these two compounds are the result of frequent detection at low concentrations. The large number of detections of these two compounds at low concentrations may be the result of some possible random contamination during sampling or may simply reflect typical environmental concentrations resulting from either natural or anthropogenic sources. Chloromethane has many natural sources, and some of the low concentrations of this compound could be natural in origin (Lovelock, 1975; Palmer, 1976; Inn and others, 1981; Harper, 1985; Wuosmaa and Hager, 1990).

Table 12. Frequencies of detection of individual volatile organic compounds at various assessment levels

[μg/L, micrograms per liter; --, not applicable]

Compound	Percent detection			Detection frequency ratio[1]
	No assessment level	Assessment level of 0.05 μg/L	Assessment level of 0.2 μg/L	
Trichloromethane	11.9	6.7	4.3	2.8
1,2,4-Trimethylbenzene	9.6	2.6	0.4	24
Chloromethane	7.3	1.7	0.1	73
Methylbenzene	5.6	3.5	1.1	5.1
Tetrachloroethene	5.5	2.9	1.7	3.2
1,1,1-Trichloroethane	3.4	1.5	1.1	3.1
Methyl *tert*-butyl ether	3.3	3.0	2.2	1.5
1,3-Dimethylbenzene/1,4-Dimethylbenzene	2.8	0.4	0	--
Dichloromethane	2.1	1.0	0.6	3.5
Benzene	2.0	0.5	0.3	6.7
Dichlorodifluoromethane	1.9	1.7	1.2	1.6
Trichloroethene	1.8	1.3	0.8	2.3
1,2-Dibromo-3-chloropropane	1.3	1.2	1.1	1.2
Bromodichloromethane	1.1	0.7	0.4	2.8
Tribromomethane	1.0	0.3	0.2	5.0
1,2-Dichloropropane	1.0	0.9	0.8	1.3
1,2-Dimethylbenzene	0.7	0.2	0	--
Trichlorofluoromethane	0.7	0.5	0.4	1.8
Diisopropyl ether	0.7	0.5	0.2	3.5
1,2,3-Trichloropropane	0.7	0.7	0.6	1.2
Ethenylbenzene	0.7	0.1	0	--
1,4-Dichlorobenzene	0.7	0.1	0.1	7.0
Chlorobenzene	0.7	0.1	0.1	7.0
1,1-Dichloroethane	0.7	0.4	0.3	2.3
Tetrachloromethane	0.6	0.4	0.3	2.0
Chlorodibromomethane	0.6	0.4	0.4	1.5
Ethylbenzene	0.5	0.2	0.1	5.0
1,3-Dichlorobenzene	0.4	0.1	0	--
1,1-Dichloroethene	0.4	0.2	0.1	4.0
(1-Methylethyl) benzene	0.3	0.1	0.1	3.0

Table 12. Frequencies of detection of individual volatile organic compounds at various assessment levels–Continued

[µg/L, micrograms per liter; --, not applicable]

Compound	Percent detection			Detection frequency ratio[1]
	No assessment level	Assessment level of 0.05 µg/L	Assessment level of 0.2 µg/L	
tert-Amyl methyl ether	0.3	0.3	0.1	3.0
Chloroethane	0.2	0.2	0.1	2.0
cis-1,2-Dichloroethene	0.2	0.2	0.1	2.0
1,2-Dichloroethane	0.2	0.2	0.2	1.0
n-Propylbenzene	0.2	0.1	0.1	2.0
1,2-Dibromoethane	0.2	0.2	0.2	1.0
1,2-Dichlorobenzene	0.2	0.1	0	--
n-Butylbenzene	0.1	0.0	0	--
Naphthalene	0.1	0.1	0.1	1.0
1,1,2-Trichloro-1,2,2-trifluoroethane	0.1	0.1	0.1	1.0
trans-1,2-Dichloroethene	0.1	0.1	0.1	1.0
Chloroethene	0.1	0.1	0.1	1.0
2-Propenal	0	0	0	--
2-Propenenitrile	0	0	0	--
Hexachloroethane	0	0	0	--
Bromomethane	0	0	0	--
1,1,2-Trichloroethane	0	0	0	--
1,2,4-Trichlorobenzene	0	0	0	--
trans-1,3-Dichloropropene	0	0	0	--
cis-1,3-Dichloropropene	0	0	0	--
Hexachlorobutadiene	0	0	0	--
Bromoethene	0	0	0	--
Ethyl *tert*-butyl ether	0	0	0	--
1,2,3-Trichlorobenzene	0	0	0	--

[1] Computed by dividing percent detection at no assessment level by percent detection at an assessment level of 0.2 µg/L.

Detections of Mixtures of VOCs Using No Assessment Level

An analysis was performed to determine the most common mixtures of VOCs in ground water from domestic wells. This analysis was performed using no assessment level because uncensored data contains the most information on low VOC concentrations. Harmful human health effects due to low concentrations of many chemicals include chemical sensitivity, endocrine disruption, and cancer (Hasegawa and others, 1994; Ashford and Miller, 1998). Many studies have demonstrated the toxicity and carcinogenicity of individual VOCs with respect to human health (Sadik and Witt, 1999), but few studies have been performed to date that examine multi-compound mixtures of VOCs and their effects on health (Yang, 1994). However, mixtures are a common mode of occurrence for many VOCs.

One or more VOCs occurred in 32 percent of samples when no assessment level was applied. Mixtures of two or more VOCs occurred in 16 percent of samples when no assessment level was applied. Therefore, about one-half of all detections of VOCs, using no assessment level, occurred as a mixture of two or more VOCs. Figure 14 illustrates detection frequency and number of compounds detected using no assessment level. Note the increased detection frequencies when no assessment level is applied compared to an assessment level of 0.2 µg/L (fig. 2).

The 10 most frequently occurring mixtures consisted of two VOCs (table 13). Three-compound mixtures also were fairly common and occurred in about 4 percent of samples. Mixtures of four and more VOCs occurred in less than 1 percent of the samples. VOCs used primarily as solvents comprised the majority of compounds in the 10 most frequently occurring mixtures (table 13). However, one refrigerant, one VOC used in organic synthesis, and several gasoline hydrocarbons also were present in the 10 most frequently occurring mixtures (table 13).

The method for determining mixtures and their occurrence consisted of counting the number of times that two or more unique combinations of VOCs occurred in each sample. Any unique mixture of two or more VOCs in a sample was counted as an occurrence of that mixture. For example, if a sample contained

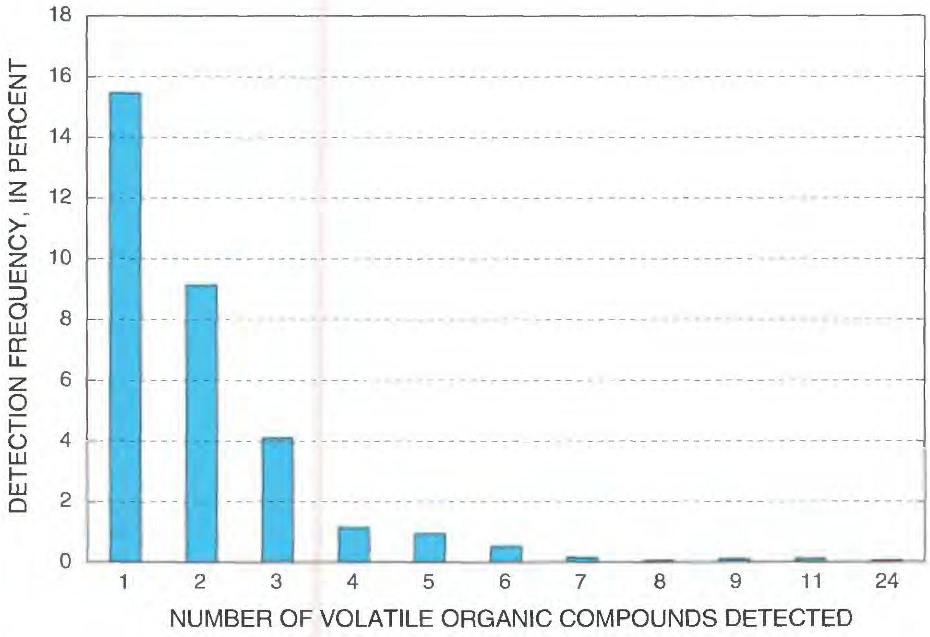


Figure 14. Detection frequency versus number of volatile organic compounds detected using no assessment level.

Table 13. Top 10 most frequently occurring mixtures of volatile organic compounds using no assessment level

Compounds in mixture	Predominant use	Number of occurrences of mixture	Frequency of detection (percent)
Trichloromethane[1] Methylbenzene	Trihalomethane Gasoline hydrocarbon	33	1.7
Trichloromethane[1] Tetrachloroethene	Trihalomethane Solvent	32	1.7
Trichloromethane[1] 1,2,4-Trimethylbenzene	Trihalomethane Organic synthesis	32	1.7
Trichloromethane[1] Chloromethane	Trihalomethane Refrigerant	32	1.7
Methylbenzene Tetrachloroethene	Gasoline hydrocarbon Solvent	30	1.6
Trichloromethane[1] 1,1,1-Trichloroethane	Trihalomethane Solvent	29	1.5
Chloromethane 1,2,4-Trimethylbenzene	Refrigerant Organic synthesis	29	1.5
Trichloromethane[1] Methyl *tert*-butyl ether	Trihalomethane Oxygenate	24	1.2
Bromodichloromethane[1] Trichloromethane[1]	Trihalomethane Trihalomethane	21	1.1
Tetrachloroethene 1,1,1-Trichloroethane	Solvent Solvent	19	1.0

[1] Also classified as a solvent or as a VOC used in organic synthesis.

three VOCs, referred to as VOC1, VOC2, and VOC3, the four mixtures in this sample would be:

1. VOC1 + VOC2,
2. VOC1 + VOC3,
3. VOC2 + VOC3, and
4. VOC1 + VOC2 + VOC3.

Each combination of VOCs in each sample was counted as a different mixture. Frequency of occurrence of the mixture (in percent) was determined by dividing the number of times a mixture occurred by the number of samples, multiplied by 100.

None of the compounds in the mixtures in table 13 are known to be direct transformation products of one another. Tetrachloroethene and 1,1,1-trichloroethane are both solvents and have some similar physical/chemical properties and thus might have similar environmental behavior characteristics. Likewise, the THMs bromodichloromethane and trichloromethane share similar physical/chemical properties, and thus also might have similar environmental behavior characteristics. The occurrence of bromodichloromethane and trichloromethane together could be the result of treatment of domestic wells using shock chlorination, which is explained in more detail later.

Some of the VOCs in table 13 might occur together because of their occurrence in on-site septic systems. As will be discussed later, an important possible point source of VOCs near the home is the septic system. Many household products contain VOCs and some VOCs have been found in septic systems.

Potential Sources of VOCs and Factors Related to VOC Occurrence

There are many potential sources of VOCs to ground water in domestic wells. It is likely that some VOCs occur in domestic wells because of use in domestic products, which then become sources of VOCs to shallow ground water near the domestic well. Relational analyses can provide insight into the hydrogeologic factors and processes that affect and control the transport and fate of VOCs in ground water. They also may provide insight into the geographic distribution of VOC occurrences, and possible anthropogenic sources of VOCs to ground water.

Potential Sources of VOCs in Ground Water from Domestic Wells

The USEPA, in conjunction with a State workgroup, has investigated potential point sources of contaminants (U.S. Environmental Protection Agency, 2000b). A list of potential sources of ground-water contamination was developed by querying States about the major sources of contamination to ground water (U.S. Environmental Protection Agency, 2000b). Some of the major sources of contaminants identified by the USEPA could be point sources near the home including underground storage tanks (USTs), septic systems, fertilizer applications, spills, pesticide applications, aboveground storage tanks (ASTs), pipelines, and sewer lines. USTs were the most commonly cited potential source of contaminants to ground water (U.S. Environmental Protection Agency, 2000b).

Although USTs are most frequently found in urban areas, some rural homes have USTs for storing heating oil, gasoline, or diesel fuel for domestic or agricultural purposes (Wisconsin Department of Natural Resources, 2000). Leakage from these domestic UST systems could be a significant source of ground-water contamination to domestic wells (Wisconsin Department of Natural Resources, 2000). The most common causes of leaks from USTs are faulty installation and corrosion of tanks and pipelines (U.S. Environmental Protection Agency, 2000b). Some homes in rural areas also have ASTs for storing gasoline, diesel fuel, or heating oil for domestic or agricultural purposes. ASTs and USTs used for storing heating oil and/or motor fuels have been identified as sources of petroleum hydrocarbon VOCs to domestic water wells (Wisconsin Department of Natural Resources, 2000).

Septic systems were listed by States as the second most important potential source of groundwater contamination. Septic systems are common in rural areas. For example, in Montana there are 126,000 individual on-site septic systems used by 252,000 people (U.S. Environmental Protection Agency, 2000b). U.S. households discharge 3.5 billion gallons of liquid into septic systems each day (U.S. Environmental Protection Agency, 2000b).

Septic systems include a buried tank for holding wastewater from the home (influent) and a fluid distribution system or leachfield for distributing liquid from the septic tank (effluent). The primary purpose of the septic tank is to hold influent coming from the home, to allow settlement or flotation of suspended solids and to allow for digestion and disintegration of solid matter by bacterial actions. Effluent from the septic tank is distributed to the leachfield, where it is discharged into relatively permeable leach-bed material. The effluent then comes into contact with the surrounding soil where microorganisms or other natural degradation processes degrade the organic matter.

Improperly designed, maintained, or operated septic systems can result in ground-water contamination in the vicinity of the system, especially if effluent from the leachfield reaches shallow ground water before the organic materials have completely degraded (U.S. Environmental Protection Agency, 2000b). Ground-water contamination resulting from incomplete degradation of organic material from septic-tank effluent can occur as a result of a variety of factors such as leaking tanks, poorly or improperly constructed tanks or leachfields, inadequate depth to water table, or highly permeable soils in the area of the leachfield.

Several studies have examined the presence of VOCs in the fluid in septic tanks (septage), in effluent from septic tanks (effluent), or in shallow ground water in areas where numerous septic systems are located. Viraraghavan and Warnock (1976) found that the concentrations of soluble organic carbon (SOC) in shallow ground water below existing septic systems were lower than in the septic-tank effluent. However, the concentrations were substantially higher than background concentrations indicating input of SOC to shallow ground water from the septic system. DeWalle and others (1985) found five VOCs present—methylbenzene, dichloromethane, trichloromethane, tetrachloroethene, and ethylbenzene—in samples of septic-tank influent and effluent from a community septic tank serving 91 homes in a subdivision of Tacoma, Washington. Viraraghavan and Hashem (1986) found bromodichloromethane, benzene, and dichloromethane in the septage (liquids and/or solids within the septic tank) and septic-tank effluent from a house in Regina, Canada, but methylbenzene only was found in the septage.

Ayres Associates (1993) analyzed VOCs in samples of septage and septic-tank effluent beneath the leachfield of many homes in several Florida counties and in samples of shallow ground water beneath a newer subdivision in Florida where all of the homes have septic systems. The samples were analyzed for 35 VOCs, with laboratory reporting levels ranging from 1 to 50 μg/L. Eight VOCs were detected above laboratory reporting levels in septage: methylbenzene, total xylenes, 1,4-dichlorobenzene, trichloromethane, dichloromethane, bromodichloromethane, 1,1-dichloroethane, and 1,1,1-trichloroethane. Only four VOCs were detected above laboratory reporting levels in septic-tank effluent: methylbenzene, trichloromethane, dichloromethane, and 1,4-dichlorobenzene. Methylbenzene was detected in the septic-tank effluent of every home sampled and in nearly every sample. Trichloromethane was the next most commonly detected VOC in septic-tank effluent, followed by dichloromethane. Bromodichloromethane and 1,4-dichlorobenzene were detected in the septic-tank effluent of only one home. Of the shallow ground water analyzed in the Florida study, only one sample from one well contained a VOC, trichloromethane, which was detected at a concentration of 1.8 μg/L.

Some of the VOCs detected in the previously cited studies also were found in ground water from domestic wells sampled for this report. Trichloromethane, which was found in shallow ground water beneath a newer subdivision in Florida (Ayres Associates, 1993), was the most frequently detected VOC in this analysis (fig. 11) and has been commonly found in septic-tank effluent. There are several other possible sources of trichloromethane in domestic well water, some are natural and some are anthropogenic.

Natural sources of trichloromethane include biomass burning (Lobert and others, 1999) and formation in spruce forest soils (Haselmann and others, 2000). Areas of wood degradation and soils with humic layers can emit, possibly from degradation of organic substances, up to 1,000 nanograms of trichloromethane per square meter per hectare (Hoekstra and others, 2001). If not volatilized from soil, trichloromethane is expected to leach to ground water due to its poor adsorption to soils. However, the quantitative contribution of natural sources to measured concentrations of trichloromethane in ground water is unknown. In addition, trichloromethane is a transformation by-product of tetrachloromethane, which is primarily used as a solvent. Major processes of the transformation of tetrachloromethane to trichloromethane include anaerobic biodegradation (Parsons and others, 1985; Curtis and Reinhard, 1994) and abiotic transformation in an anaerobic environment (hydrogenolysis) (Criddle and McCarty, 1991).

Some sources of trichloromethane probably are anthropogenic. Household bleach, of which sodium hypochlorite is an active ingredient, often is used to disinfect a domestic well that has been contaminated by bacteria (U.S. Environmental Protection Agency, 1993). A solution of bleach and water is added directly to the well to destroy the bacteria in a process often referred to as shock chlorination. The addition of bleach to ground water adds free chlorine, which then can result in the formation of THMs through reactions between free chlorine and naturally occurring organic material in the water (Trussell and Umphres, 1978; Alawi and others, 1994). Trichloromethane might form through the same reactions during the use of household bleach in washing machines. Wastewater discharged from the washing machine to a septic system may enter shallow ground water near the domestic well.

Methylbenzene, tetrachloroethene, dichloromethane, bromodichloromethane, 1,1,1-trichloroethane, 1,1-dichloroethane, and benzene also were found in septage or septic-tank effluent. These VOCs also were among the 20 VOCs most frequently detected in samples in this analysis and many are solvents (fig. 11). Chlorinated solvents that are used as degreasing agents in cleaning septic-tank pipes and leachfield lines (Pankow and Cherry, 1996) also may be a contaminant source to domestic well water.

Although found frequently in septage and septic-tank effluent, the presence of many of the same VOCs in ground water from domestic wells does not prove that the source of the VOCs is the septic system. However, many types of household products containing VOCs are disposed into septic systems. If a septic system is improperly designed, maintained, or operated, there is an increased likelihood that these VOCs could end up in shallow ground water near the well, especially if the well is located close to, or is hydraulically connected to, the septic system.

All of the seven most frequently detected VOCs (fig. 11) are ingredients in consumer products that could be used in and around households and have been found in septic systems. Three of these seven VOCs (methylbenzene, tetrachloroethene, and 1,1,1-trichloroethane) are ingredients in a wide variety of products. For example, tetrachloroethene is predominantly used as a solvent (table 6), but also is used in products such as automotive cleaners and degreasers, household cleaners, lubricants, pesticides, and products used for personal hygiene (table 14).

One important observation regarding the use of VOCs in household products is that the 18 VOCs not detected in domestic wells either are not known to be ingredients in any consumer product category or are ingredients in only a few of them (table 14). For example, 5 of these 18 VOCs (bromoethene, 2-propenal, ethenylbenzene, 1,2,3-trichlorobenzene, and 1,1,2-trichlorethane) are not known to be ingredients in any consumer product (table 14) although the information concerning VOCs in consumer products given here may be incomplete. On the other hand, the seven most frequently detected VOCs have many uses in a variety of household products (table 14).

Relations of VOCs to Hydrogeologic and Anthropogenic Variables

Several studies have examined relations between VOCs and hydrogeologic and anthropogenic variables. A review of some previous studies and results on this subject is provided, and possible relations that would be anticipated or expected based on hydrogeologic principles and chemical and environmental processes are discussed. The examination of possible relations was performed for VOCs by use groups because compounds with similar uses likely will have similar sources. When more VOC chemical data and ancillary data from domestic wells become available, relational analyses will be performed on this data set to provide additional insight into the distribution, transport, and sources of VOCs in ground water that supplies domestic wells.

Fumigants

The probability of detecting a fumigant in ground water likely decreases with increasing depth to the top of the screened interval in the well, or well depth. Barbash and Resek (1996) report that results from a variety of studies of pesticide detections in ground water indicated that well depth was the factor most commonly correlated with pesticide detections. In most of these pesticide studies, well depth was negatively correlated with pesticide detection frequency. This negative correlation between pesticide detection and well depth is the result of the increased time required for a pesticide applied at the surface, such as a fumigant, to reach deeper screened intervals. As time increases, processes like hydrodynamic dispersion, sorption, transformation, and volatilization increase the probability that the pesticide concentration will decrease below detectable concentrations.

The probability of detecting a fumigant likely is higher in ground water from unconsolidated aquifers compared to consolidated aquifers. Barbash and Resek (1996) report that results from most studies showed higher detection frequencies of pesticides in unconsolidated aquifers compared to bedrock or consolidated aquifers. In general, consolidated aquifers, where overlain by unconsolidated aquifers, tend to be deeper and less vulnerable to contamination from surface sources (Barbash and Resek, 1996). However, consolidated aquifers at or near the land surface, especially if composed of karst limestone or fractured bedrock, can be just as vulnerable or more vulnerable than unconsolidated aquifers.

The probability of detecting a fumigant in ground water likely is higher in areas of predominant agricultural land use relative to urban land use in the area surrounding the well. Barbash and Resek (1996) reported that studies have indicated higher pesticide detection frequencies in ground water underlying agricultural areas compared to non-agricultural areas, and the occurrence of heavily used fumigants has been correlated with use pattern. Because fumigants are most extensively used in select agricultural practices, the likelihood of occurrence of VOCs in ground water underlying agricultural areas is higher.

Table 14. Consumer usage of 18 volatile organic compounds not detected and 7 volatile organic compounds most frequently detected in rural, untreated, self-supplied domestic well water

[VOCs, volatile organic compounds; NA, not applicable]

VOC	Predominant use	Architectural	Automotive			Fuel	Household cleanser	Insecticide/ pesticide/ fumigant	Lubricant	Personal hygiene	Protectant/ sealant	Refrigerant	Solvent
			Cleaner	Coating	Degreaser								
							18 VOCs Not Detected in Rural, Self-Supplied Domestic Well Water						
Bromomethane[1]	Fumigant							X					
cis-1,3-Dichloropropene[2]	Fumigant							X					
trans-1,3-Dichloropropene[2]	Fumigant							X					
n-Butylbenzene[1]	Gasoline hydrocarbon					X							X
1,2-Dimethylbenzene[1]	Gasoline hydrocarbon					X		X					
1,3-Dimethylbenzene[1]/ 1,4-Dimethylbenzene	Gasoline hydrocarbon					X							
Bromoethene[2,3]	Organic synthesis												
Hexachlorobutadiene[1,2]	Organic synthesis												X
2-Propenal[3]	Organic synthesis												
2-Propenenitrile[3]	Organic synthesis							X					
Ethenylbenzene[3]	Organic synthesis												
1,2,3-Trichlorobenzene[3]	Organic synthesis												
Ethyl *tert*-butyl ether	Oxygenate					X							
1,2-Dichlorobenzene[2]	Solvent							X	X				
1,3-Dichlorobenzene[2]	Solvent								X				

Table 14. Consumer usage of 18 volatile organic compounds not detected and 7 volatile organic compounds most frequently detected in rural, untreated, self-supplied domestic well water–Continued

[VOCs, volatile organic compounds; NA, not applicable]

VOC	Predominant use	Architectural	Automotive			Fuel	Household cleanser	Insecticide/ pesticide/ fumigant	Lubricant	Personal hygiene	Protectant/ sealant	Refrigerant	Solvent
			Cleaner	Coating	Degreaser								
18 VOCs Not Detected in Rural, Self-Supplied Domestic Well Water—Continued													
Hexachloroethane[2]	Solvent												X
1,2,4-Trichlorobenzene[2]	Solvent							X	X				
1,1,2-Trichloroethane[2]	Solvent												
7 VOCs Most Frequently Detected in Rural, Self-supplied Domestic Well Water													
1,2-Dibromo-3-chloropropane[1,4]	Fumigant							X					
Methylbenzene[4,5]	Gasoline hydrocarbon		X	X	X	X		X	X	X	X		X
Methyl *tert*-butyl ether	Oxygenate					X							
Dichlorodiflouromethane[1,4]	Refrigerant												X
Tetrachloroethene[5]	Solvent	X	X	X	X		X	X	X	X	X	X	X
1,1,1-Trichloroethane[5]	Solvent	X	X	X			X	X	X		X		X
Trichloromethane[1,6]	Trihalomethane						X	X				X	X

[1] Vershueren, 1983.

[2] Lewis, 1993.

[3] Prager, 1995.

[4] Montgomery, 1991.

[5] California Air Resources Board, 2000.

[6] Trichloromethane also can be classified as a solvent or as a VOC used in organic synthesis.

The probability of detecting a fumigant in ground water likely increases with increasing soil particle size. A study by Teso and others (1996) demonstrated a relation between increased soil particle size and increased probability of detecting 1,2-dibromo-3-chloropropane. Particle size affects soil permeability and other hydrologic properties of the soil including saturated hydraulic conductivity and water-holding capacity, which in turn controls transport of fumigants like 1,2-dibromo-3-chloropropane to ground water (Teso and others, 1996).

Gasoline Hydrocarbons

The probability of detecting a gasoline hydrocarbon compound in ground water likely decreases with increasing depth to the top of the screened interval in the well. As a group, gasoline hydrocarbons have a relatively low average half-life (fig. 11) and may biodegrade relatively quickly in the environment, especially in aerobic conditions (Howard and others, 1991). A negative correlation between gasoline hydrocarbon detection frequency and depth to the top of the screened interval likely would result from the increased time required for a compound to reach deeper screened intervals. As time increases, physical and chemical processes, especially transformation, increase the probability that the concentration of gasoline hydrocarbons will decrease below detectable concentrations.

The probability of detecting a gasoline hydrocarbon compound in ground water likely is higher in areas of predominant urban land use relative to agricultural land use in an area surrounding the well. Vowinkel and Battaglin (1989) and Vowinkel (1991) found that the detection frequency of purgeable organic compounds was higher in urban land-use areas compared to agricultural land-use areas. Moran and Davis (1998) found that the detection frequency of one of nine selected VOCs, two of which were gasoline hydrocarbons (benzene and toluene), was higher in urban areas compared to non-urban areas.

Organic Synthesis

The probability of detecting a compound used for organic synthesis in ground water likely decreases with increasing depth to the top of the screened interval in the well. The increased time required for an organic synthesis compound to reach a deeper screened interval would allow processes like hydrodynamic dispersion, sorption, transformation, and volatilization to increase the probability that the concentration would decrease below detectable concentrations.

Gasoline Oxygenates

The probability of detecting an oxygenate likely increases as population density near the well increases and likely is higher in areas of predominant urban land use relative to agricultural land use in an area near the well. Most use of ether oxygenates today is in larger metropolitan areas in the northeast United States and in California, and the most frequently used oxygenate is MTBE. The areas of high oxygenate use also are areas with higher population densities. Because oxygenate use is highest in urban areas and areas of high population density, there are many more potential sources in these areas and a higher probability of occurrence in ground water. Studies have shown a positive correlation between MTBE occurrence in ground water and both MTBE use and population density (Moran, Halde, and others, 1999; Squillace and Moran, 2000; Moran and others, 2002). Because MTBE is highly soluble in water, does not substantially partition to organic carbon in aquifer material, and biodegrades slowly relative to gasoline hydrocarbons, it would be expected to occur more frequently in ground water than other gasoline components.

Refrigerants

The probability of detecting a refrigerant in ground water likely decreases with increasing depth to the top of the screened interval in the well. Halogenated aliphatic compounds like refrigerants, although generally resistant to biodegradation and other removal processes like volatilization and hydrolysis, will degrade via various biotic and abiotic processes (McCarty and others, 1992). The increased time required for a refrigerant to reach a deeper screened interval in a well would allow processes like hydrodynamic dispersion, sorption, transformation, and volatilization to increase the probability that the concentration would decrease below detectable levels.

Solvents

The probability of detecting a solvent in ground water likely decreases with increasing depth to the top of the screened interval in the well. As depth to the top of the screened interval increases, the time required for a contaminant to reach the screened interval also increases. This increased time factor allows for increased attenuation of the concentrations due to natural loss processes such as biodegradation, sorption, dispersion, and volatilization. Halogenated aliphatic compounds like solvents, although generally resistant to removal processes like biodegradation, volatilization, and hydrolysis, will degrade via various biotic and abiotic processes (McCarty and others, 1992).

The probability of detecting a solvent in ground water is likely higher in areas of predominant urban land use than in agricultural land use in an area overlying the well. Large quantities of solvents have been produced and used by a wide variety of sectors in our modern society (Pankow and Cherry, 1996). Most of the industrial and commercial activities that use solvents are performed in urban areas. Because solvents are used more widely in urban activities compared to agricultural activities, more sources of solvents to ground water are expected in urban areas.

Trihalomethanes

The probability of detecting a trihalomethane in ground water is likely higher in areas of predominant urban land use relative to agricultural land use in an area surrounding the well. Trihalomethanes are known to be by-products of disinfection of drinking water with chlorine via haloform reactions with naturally occurring organic materials in water (Trussell and Umphres, 1978; Alawi and others, 1994). Disinfection procedures are most commonly performed on drinking water supplied by community water systems in urban areas. Thus, urban areas would be associated with more sources of disinfection-treated water. Since trihalomethanes commonly have been detected in septic tank effluent, there may be a correlation between the distance from domestic wells to septic systems, or ground-water flow direction, and the presence of trihalomethanes in domestic wells.

SUMMARY AND CONCLUSIONS

Samples of untreated ground water from 1,926 rural, self-supplied domestic wells were analyzed for volatile organic compounds (VOCs) during 1986-99. This information was used to characterize the occurrence and status of VOCs in domestic well water. The samples were either collected as part of the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program occurrence-assessment studies or were compiled by NAWQA from existing ambient ground-water or source-water-quality monitoring programs conducted by local, State, and other Federal agencies. Water samples were collected at the wellhead prior to treatment or storage. In most samples, 55 target VOCs were analyzed, and occurrence and status information generally was computed at an assessment level of 0.2 μg/L.

Samples of ground water from rural, self-supplied domestic wells often did not contain VOCs. Only 12 percent of the 1,926 samples had a detection of at least one VOC at an assessment level of 0.2 μg/L. Samples with detections of at least one VOC were collected from wells located in 31 of 39 States.

When grouped by predominant use, solvents were the most frequently detected VOC group with detections in 4.6 percent of samples at an assessment level of 0.2 μg/L. The THMs were the second most frequently detected VOC group with detections in about 4 percent of samples. With the exception of compounds used in organic synthesis, detection frequencies of VOCs by groups are proportional to the average half-life of compounds in the group. When the organic synthesis group is excluded from the analysis, there is a good correlation between the detection frequency of VOCs by groups and average half-life of compounds in the group. The geographic distribution of detections of some VOC groups, such as fumigants and oxygenates, appears to be related to the use pattern of compounds in that group.

Of the 54 VOCs with data, 36 had concentrations at or above the assessment level of 0.2 μg/L in at least one sample. The seven VOCs that had the highest detection frequencies included, in order of decreasing detection frequency, trichloromethane, methyl *tert*-butyl ether, tetrachloroethene, dichlorodifluoromethane, 1,1,1-trichloroethane, methylbenzene, and 1,2-dibromo-3-chloropropane. Only 1.4 percent of samples had one or more VOC concentrations that exceeded a drinking-water standard, a health criterion, or both. Only 0.1 percent of samples had VOC concentrations that exceeded a taste/odor threshold. The six VOCs that exceeded an MCL at least once included: 1,2-dibromoethane, 1,1-dichloroethene, 1,2-dichloropropane, trichloroethene, 1,2-dibromo-3-chloropropane, and tetrachloroethene. Sixteen of the 28 total exceedances of an MCL were by the fumigant 1,2-dibromo-3-chloropropane. The MCL for 1,2-dibromo-3-chloropropane is relatively low when compared to other VOCs. Most of the exceedances of 1,2-dibromo-3-chloropropane were in the Central Valley of California where this compound was used extensively as a soil fumigant prior to its ban in 1985.

Mixtures of two or more compounds were a common mode of occurrence of VOCs. Mixtures occurred in one-half of all samples where at least one VOC was detected when no assessment level was applied. The most frequently detected mixtures were two-compound mixtures. Solvents were the most common VOCs found in mixtures, but compounds from the gasoline hydrocarbon, organic synthesis, and refrigerant groups also were found. The source of most mixtures is not clearly understood, but septic systems could be a source for many VOCs.

Potential point sources of VOCs near domestic wells are numerous and include underground storage tanks (USTs), aboveground storage tanks (ASTs), septic systems, fertilizer applications, spills, pesticide applications, pipelines, and sewer lines. Releases from USTs and ASTs that hold gasoline, diesel fuel, or heating oil have the potential to be major point sources of contaminants to domestic wells. Shock chlorination may be a source of trichloromethane and other THMs in some domestic wells. VOCs frequently are ingredients in household products, many of which have been found in septic systems. Septic systems are believed to be an important source of contaminants to domestic wells, but extensive research on this subject does not exist.

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