Approach to an Assessment of Volatile Organic Compounds in the Nation's Ground Water and Drinking-Water Supply Wells

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

Open-File Report 2005–1452

U.S. Department of the Interior
Gale A. Norton, Secretary

U.S. Geological Survey
P. Patrick Leahy, Acting Director

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. (http://www.usgs.gov/). Information on the quality of the Nation's water resources is of critical interest to the USGS because it is so integrally linked to the long-term availability of water that is clean and safe for drinking and recreation and that is suitable for industry, irrigation, and habitat for fish and wildlife. Escalating population growth and increasing demands for the multiple water uses make water availability, now measured in terms of quantity and quality, even more critical to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program to support national, regional, and local information needs and decisions related to water-quality management and policy. (http://water.usgs.gov/nawqa/). 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 and priorities. 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. (http://water.usgs.gov/nawqa/nawqamap.html). 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. (http://water.usgs.gov/nawqa/natsyn.html).
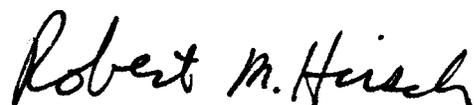
Robert M. Hirsch
Associate Director for Water

Contents

Figures

Tables

Conversion Factors

Multiply	By	To obtain
Length		
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
kilometer (km)	0.5400	mile, nautical (nmi)
meter (m)	1.094	kilometer (km)
Area		
square kilometer (km^2)	247.1	yard
Density		
gram per cubic centimeter (g/cm^3)	62.4220	pound per cubic foot

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F=(1.8×°C)+32$$

Study Unit Abbreviations, Other Abbreviations, and Acronyms

ACAD	Acadian-Pontchartrain Drainages
ACFB	Apalachicola-Chattahoochee-Flint River Basins
ALBE	Albemarle-Pamlico Drainages
ALMN	Allegheny-Monongahela River Basins
CAZB	Central Arizona Basins
CCPT	Central Columbia Plateau
CNBR	Central Nebraska Basins
CONN	Connecticut, Housatonic, and Thames River Basins
COOK	Cook Inlet Basin
DELR	Delaware River Basin
DLMV	Delmarva Peninsula
EIWA	Eastern Iowa Basins
GAFL	Georgia-Florida Coastal Plain Drainages
GRSL	Great Salt Lake Basins
HDSN	Hudson River Basin
HPGW	High Plains Regional Ground Water Study
KANA	Kanawha-New River Basin
LERI	Lake Erie-Lake St. Clair Drainages
LINJ	Long Island-New Jersey Coastal Drainages
LIRB	Lower Illinois River Basin
LSUS	Lower Susquehanna River Basin
LTEN	Lower Tennessee River Basin
MIAM	Great and Little Miami River Basins
MISE	Mississippi Embayment
MOBL	Mobile River Basin

Study Unit Abbreviations, Other Abbreviations, and Acronyms—Continued

NECB	New England Coastal Basins
NROK	Northern Rockies Intermontane Basins
NVBR	Nevada Basin and Range
OAHU	Oahu
OKLA	Oklahoma Ground-Water Pilot Study
OZRK	Ozark Plateaus
PUGT	Puget Sound Drainages
REDN	Red River of the North Basin
RIOG	Rio Grande Valley
SACR	Sacramento River Basin
SANA	Santa Ana River Basin
SANJ	San Joaquin-Tulare River Basins
SANT	Santee River Basin and Coastal Drainages
SCTX	South-Central Texas
SOFL	Southern Florida Drainages
SPLT	South Platte River Basin
TRIN	Trinity River Basin
UCOL	Upper Colorado River Basin
UIRB	Upper Illinois River Basin
UMIS	Upper Mississippi River Basin
USNK	Upper Snake River Basin
UTEN	Upper Tennessee River Basin
WILL	Willamette Basin
WMIC	Western Lake Michigan Drainages
YELL	Yellowstone River Basin
mg/L	Milligrams per liter
mL	Milliliters
µg/L	Micrograms per liter
µS/cm	Microsiemens per centimeter at 25 degrees Celsius
°C	Degrees Celsius
AWWARF	American Water Works Association Research Foundation
BFI	Base-flow index
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CWS	Community water system
DBCP	Dibromochloropropane
ECD	Electron capture detector
EDB	Ethylene dibromide
GC/MS	Gas chromatography/mass spectrometry
GWSI	Ground-Water Site Inventory
HBSLs	Health-Based Screening Levels
LT-MDL	Long-term method detection level

Study Unit Abbreviations, Other Abbreviations, and Acronyms—Continued

MCL	Maximum Contaminant Level
MDL	Method detection limit
MRL	Minimum reporting level
MTBE	Methyl *tert*-butyl ether
MWDSC	Metropolitan Water District of Southern California
NAWQA	National Water-Quality Assessment
NCDC	National Climate Data Center
NELAC	National Environmental Laboratory Accreditation Conference
NLCD	National Land Cover Dataset
NWQL	National Water Quality Laboratory
OBSP	Organic Blind Sample Project
PQL	Practical Quantitation Level
QA	Quality assurance
QC	Quality control
QWDATA	Water-Quality database
RCRA	Resource Conservation and Recovery Act
SDWA	Safe Drinking Water Act
STATSGO	Service State Soil Geographic
THMs	Trihalomethanes
TRI	Toxics Release Inventory
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
UST	Underground storage tank
VOC	Volatile organic compound

Approach to an Assessment of Volatile Organic Compounds in the Nation's Ground Water and Drinking-Water Supply Wells

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

Abstract

The National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey (USGS) developed an approach for a national assessment of the occurrence, status, and distribution of volatile organic compounds (VOCs) in samples of ground water from aquifer studies and in samples from drinking-water supply wells, specifically domestic and public wells. Data on VOCs in samples from aquifers and from domestic and public wells had three sources: (1) NAWQA sampling of ground water in aquifer studies and of shallow ground water in areas of agricultural or urban land use from 1993–2002, (2) retrospective data from other Federal, State, and local agencies that sampled ground water in aquifer studies from 1985–1997, and (3) sampling of ground water from public wells used as a source of drinking water from 1999–2000 (source-water survey).

Data for assessing VOCs in ground water came from the NAWQA sampling of aquifers and from retrospective data (1 and 2). Domestic wells were the most commonly sampled well type in these aquifer studies. Data for assessing VOCs in domestic well samples came from the NAWQA sampling of aquifers and shallow ground water and from retrospective data (1 and 2). Data for assessing VOCs in public well samples came from NAWQA sampling of aquifers and shallow ground water and from the source-water survey (1, 2, and 3).

Fifty-five VOCs were included in the national assessment. All ground-water samples were collected using consistent, prescribed field protocols and were analyzed using approved analytical methods. All ground-water collection activities and laboratory procedures included the collection of various quality-control samples in order to ensure the quality of the data.

Comparisons of detection frequencies and detected concentrations among individual VOCs, groups of VOCs, aquifer studies, and data sets were performed using two assessment levels: (1) an assessment level of 0.2 microgram per liter (µg/L), and (2) an assessment level of 0.02 µg/L. Selection of the 0.2-µg/L assessment level was based on historical laboratory reporting levels of VOCs used by the USGS National Water-Quality Laboratory (NWQL) prior to April 1996, and selection of the 0.02-µg/L assessment level was based on a new, low-level analytical method developed by the NWQL and used since April 1996.

Relational analyses using multivariate logistic regression were performed on VOC data from aquifers, domestic wells, and public wells to better understand the natural and anthropogenic factors that control or influence the occurrence of VOCs. Ancillary data used in the relational analyses represent a variety of anthropogenic and hydrogeologic controls on the occurrence of VOCs. For aquifers, relational analyses were performed only on NAWQA data analyzed using the new low-level analytical method for 10 frequently detected VOCs. For domestic wells, relational analyses were performed at assessment levels of 0.2 µg/L and 0.02 µg/L for 6 and 10 frequently detected VOCs at these levels. For public wells, relational analyses were performed at an assessment level of 0.2 µg/L for nine frequently detected VOCs.

Introduction

The National Water-Quality Assessment (NAWQA) Program of the United States Geological Survey (USGS) was designed to describe occurrence, status, and trends in the quality of the Nation's ground-water and surface-water resources (Gilliom and others, 1995). This was achieved through a series of local and regional assessments that when combined provide a national scale overview of distribution and trends in water-quality conditions. Another goal of the program was to link water-quality occurrence information with an understanding of the natural and human factors that affect the quality of water. By better understanding the factors that control or affect water quality, the NAWQA Program can contribute most substantially to managing, protecting, and restoring water resources (Gilliom and others, 1995).

Local water-quality assessments formed the building blocks of the NAWQA Program. These local study areas were known as Study Units. Figure 1 shows the location and distribution of Study Units (including the High Plains Regional Ground-Water Study) that sampled ground water for volatile organic compounds (VOCs) included in a national assess-

ment. Results from the NAWQA Program were synthesized using multiple local and regional assessments, including Study Unit investigations and other information, to produce periodic, comprehensive national summaries of water quality for selected contaminant groups (Gilliom and others, 1995). A national synthesis of the NAWQA Program focusing on VOCs began in 1994. The NAWQA VOC National Synthesis developed an approach for analyzing data collected or complied by the NAWQA Program for a national assessment. The main purpose of the national assessment of VOCs was to provide an improved understanding of the occurrence, status, and distribution of selected VOCs in the Nation's ground water and drinking-water supply wells, specifically domestic and public wells. The assessment also provided a preliminary understanding of natural and anthropogenic factors that affect or influence the occurrence and distribution of VOCs.

Purpose and Scope of Report

The purpose of this report is to describe the approach used to prepare a national assessment of VOCs in the Nation's ground water and drinking-water supply wells and to present supporting technical information. This report also provides documentation of the planning efforts and design undertaken for a national assessment.

Data on VOCs in samples from aquifers and from domestic and public wells had three sources: (1) NAWQA sampling of ground water in aquifer studies and of shallow ground water in areas of agricultural or urban land use from 1993–2002, (2) retrospective data from other Federal, State, and local agencies that sampled ground water in aquifer studies from 1985–1997, and (3) sampling of ground water from public wells used as a source of drinking water from 1999–2000 (source-water survey). The interpretive results of the national assessment can be found in Zogorski and others (2006).
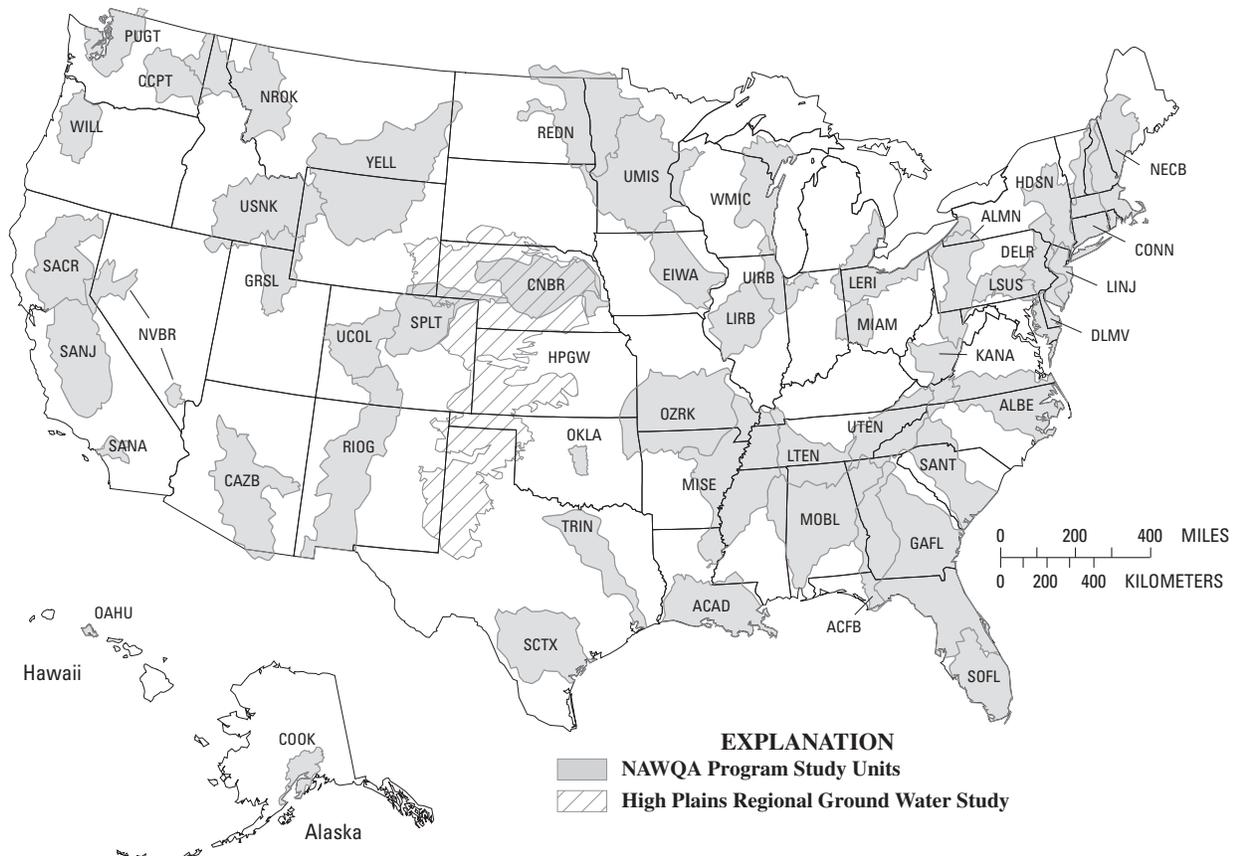
EXPLANATION

NAWQA Program Study Units

High Plains Regional Ground Water Study

Base modified from U.S. Geological Survey digital data, 1:2,000,000, 1990
Albers Equal-Area Projection
North American Datum of 1983

Figure 1.   Study Units where the National Water-Quality Assessment (NAWQA) Program has completed an occurrence survey of volatile organic compounds in aquifers.

General Information on VOCs

VOCs are important ground-water contaminants. The occurrence of VOCs in ground-water resources of the United States has been well documented (Squillace and others, 1999; Moran and others, 2002). Some VOCs, like gasoline hydrocarbons, are currently (2005) produced in billions of liters per year. In addition, the production of synthetic organic chemicals such as VOCs has been increasing, with more than an order of magnitude increase between 1945 and 1985 (Ashford and Miller, 1991). Some VOCs also have been produced for long periods of time. For example, chlorinated solvents have been produced for nearly 100 years in the United States (Pankow and Cherry, 1996).

VOCs are present in a variety of commercial and industrial chemicals and are used in a variety of commercial and industrial applications including dry cleaning, refrigeration, pest control, solvent applications, and the manufacture of plastics and pharmaceuticals. Products containing VOCs also are used extensively in households and include cosmetics, room deodorizers, deodorants, fabric softeners, paint, adhesives, cleaning and polishing products, pesticides and fumigants, solvent degreasers, refrigerants, and fuels (Bloemen and Burn, 1993; Bender and others, 1999). Some VOCs have large production volumes, long histories of production, and large usage in commerce and industry. These compounds are at substantial risk of release to the environment.

In fact, the large production and usage of some VOCs in the United States has resulted in considerable releases to the environment based on data reported in the U.S. Environmental Protection Agency's (USEPA) Toxics Release Inventory (TRI) (U.S. Environmental Protection Agency, 2003a). The TRI provides information on the release of toxic chemicals from manufacturing facilities in the United States. According to the TRI, during 2001, 4 of the 20 chemicals with the largest total on-site and off-site releases to the environment were VOCs, including toluene, styrene, xylene (mixed isomers), and *n*-hexane. During 2001, the total estimated release of these four chemicals exceeded 400 million pounds (U.S. Environmental Protection Agency, 2003a).

Although the TRI indicates large releases of VOCs to the environment, not all releases of VOCs to the environment are included in the TRI. For example, 14 of the top 29 contaminants at Superfund sites are VOCs, and a reporting of these releases is not included in the TRI (U.S. Environmental Protection Agency, 2005a). Underground storage tanks (USTs) also are a common source of VOCs to the environment, especially to ground water. VOCs commonly are found in petroleum products and in many types of hazardous wastes that are stored in USTs. Currently (2005), more than 680,000 UST systems store petroleum or hazardous wastes nationwide (U.S. Environmental Protection Agency, 2005b).

VOCs have physical and chemical properties that allow them to move between water and air and be mobile and persistent in ground water (Bender and others, 1999). Once in ground water, processes such as diffusion, advection, sorption, hydrodynamic dispersion, volatilization, and transformation may affect the occurrence, transport, and fate of VOCs. The occurrence of VOCs in ground water used for drinking water has been associated with potential human-health concerns such as short-term toxic effects like kidney or liver damage and long-term toxic effects such as carcinogenicity (U.S. Environmental Protection Agency, 2004a). Of the VOCs included in NAWQA's national assessment, 80 percent have drinking-water standards or health benchmarks established by Federal agencies.

Overview of Approach

This section provides an overview of the approach for a national assessment of VOCs. Included in this section is information on (1) VOCs selected for inclusion in the data set; (2) ground-water-quality data selected for inclusion in the data set; (3) field sampling and laboratory analytical methods; (4) field and laboratory quality-assurance protocols and quality-control procedures; and (5) computational and statistical methods used for analyses.

VOCs Selected

Fifty-five VOCs were selected for inclusion in the national assessment of VOCs. The VOCs were selected using a three-phase procedure: (1) initial screening of 130 candidate VOCs on the basis of available information; (2) laboratory studies to ascertain the feasibility of analysis of the VOCs by purge-and-trap gas chromatography/mass spectrometry (GC/MS); and (3) analysis of VOCs in ground-water and surface-water samples to determine the performance of laboratory methods on environmental samples (Bender and others, 1999). The selection of candidate VOCs involved many criteria including: (1) physical properties; (2) human cancer rating; (3) noncancer human-health risk; (4) toxicity to freshwater aquatic organisms; (5) occurrence in ground water, surface water, or drinking water; (6) potential for atmospheric ozone depletion; (7) bioconcentration in aquatic organisms; and (8) use or potential use as an oxygenate in gasoline. A detailed description of the criteria and processes used to select the 55 VOCs can be found in Bender and others (1999).

The 55 VOCs ultimately selected included compounds with (1) low molecular weights; (2) high vapor pressures; (3) low-to-medium water solubilities; (4) known or probable cancer and noncancer human-health effects; (5) known or potential toxicity to aquatic organisms; (6) known, frequent occurrence in ground water, surface water, or drinking water; (7) known importance for other reasons such as atmospheric ozone depletion or bioconcentration in aquatic organisms; and (8) use as gasoline oxygenates (Bender and others, 1999). The selected VOCs include 21 halogenated alkanes, 10 halogenated alkenes, 3 aromatic hydrocarbons, 9 alkylbenzenes, 6 halogenated aromatics, 4 ethers, 1 aldehyde, and 1 nitrile.

The 55 VOCs also can be grouped into classes based on their primary usage in commercial and industrial applications (Bender and others, 1999). Although many VOCs have multiple commercial and industrial uses, each VOC was placed into a group representing the predominant use (or origin) of the compound. The seven groups are (1) fumigants; (2) gasoline hydrocarbons; (3) gasoline oxygenates; (4) compounds used for organic synthesis; (5) refrigerants; (6) solvents; and (7) trihalomethanes (THMs). The THM group does not indicate a predominant use of these compounds but instead represents a grouping based on origin and chemical class. Although some THMs have uses in industry and commerce, the origin of most of these compounds in ground water is believed to be a result of the chlorination of drinking water (Ivahnenko and Barbash, 2004).

Table 1 lists the 55 VOCs and the group representing predominant usage of each compound. Table 1 also includes VOCs that were analyzed in samples collected by many of the Study Units but were not included in the national assessment. Acrolein was deleted from the laboratory schedules in May 1998 because of erratic and poor instrument response; however, results were reported because the NAWQA Program collected acceptable data for this compound during 1996–1998 (Bender and others, 1999).

Prior to April 1996, the three xylene isomers (*o*-xylene, *m*-xylene, and *p*-xylene) were reported together as mixed xylenes. After April 1, 1996, however, the USGS National Water-Quality Laboratory (NWQL) reported concentrations of xylene isomers as two components: (1) *o*-xylene, and (2) *m*- and *p*-xylenes combined. Results for *m*-xylene and *p*-xylene were reported as a sum because they could not be separated by the analytical methods (Bender and others, 1999). Data on the xylene isomer components in ground water indicate that each isomer appears in roughly equal concentrations in the environment. Thus, for the purposes of describing occurrence in the national assessment of VOCs, a detection of the mixed xylene group or a detection of *o*-xylene or *m*- and *p*-xylenes separately is presumed to indicate a detection of all three individual xylenes.

Ground-Water-Quality Data

Data from three main sources comprise the VOC chemical information that was available for a national assessment of VOCs: (1) data from the NAWQA Program that sampled ground water in aquifer studies and in studies of shallow ground water underlying agricultural and urban land-use areas throughout the United States during 1993–2002 as a part of Study-Unit investigations; (2) existing data from other Federal, State, and local agencies that sampled ground water in aquifer studies throughout the United States during 1985–1997 (retrospective); and (3) data from a collaborative effort of the NAWQA Program and other organizations in a national survey that sampled ground water used as a source of drinking water throughout the United States during 1999–2000 (source-water survey). Although the total time span of collection of samples for the national assessment of VOCs is large (1985–2001), the vast majority (87 percent) of samples were collected between 1991 and 2001. Thus, the data are considered to represent a 10-year examination of water quality for the Nation's ground water and drinking-water supply wells.

Table 2 lists the number of wells by data source and well type for the entire data set used in a national assessment of VOCs. For some analyses, data from a survey of drinking water in 12 New England and Mid-Atlantic States also were used. This data set is explained in more detail in the section titled "VOC Data Used for Comparison to Drinking Water".

NAWQA Data

The NAWQA Program used aquifer studies as a major element of the design of the Study Unit investigations. An aquifer study is an areally distributed, randomly selected set of sampling points in an aquifer or hydrogeologic unit of interest. Sometimes sites in an aquifer study were selected by various characteristics of an area, such as land use or hydrogeologic setting. In these cases, the random, stratified selection of sampling sites in the area was performed using computer software developed by the USGS (Scott, 1990).

Three types of studies were designed for sampling ground water in Study Units: (1) Study-Unit surveys (referred to here as aquifer studies), (2) shallow ground-water studies, and (3) flowpath studies. As previously mentioned, aquifer studies were the main focus of a national assessment of VOCs. Shallow ground-water studies were designed to sample shallow ground water in areas of predominantly agricultural or urban land use in order to link natural and human factors with water-quality conditions. Flowpath studies were designed to determine the source, transport, and ultimate fate of ground-water contaminants at a local scale and to understand interactions between surface water and ground water. The majority of data from the shallow ground-water studies and flowpath studies were not included in the national assessment of VOCs because they were designed for special objectives rather than general occurrence assessments.

Some data from domestic wells, sampled as part of shallow ground-water studies, were included in the national assessment of VOCs because one of the goals of the national assessment was to determine water quality from domestic wells without regard to overlying land use. In addition, data from shallow ground-water studies in urban areas were used in the national assessment of VOCs, in a limited manner, to link ground-water-quality conditions to natural and human factors. The data on VOCs in ground water from beneath agricultural land-use areas were too limited in geographic extent to be useful in linking ground-water-quality conditions to natural and human factors.

Table 1. Predominant uses for the 55 VOCs included in a national assessment and for other VOCs analyzed in some samples.

[non-emphasized VOCs are shown in gray shading]

			Use group			
Fumigants	**Gasoline hydrocarbons**	**Gasoline oxygenates**	**Organic synthesis**	**Refrigerants**	**Solvents**	**Trihalomethanes[1]**
Bromomethane	Benzene	tert-Amyl methyl ether	Acrolein	Dichlorodifluoromethane	Carbon tetrachloride	Bromodichloromethane
Dibromochloropropane	n-Butylbenzene	Diisopropyl ether	Acrylonitrile	Trichlorofluoromethane	Chlorobenzene	Bromoform
1,4-Dichlorobenzene	Ethylbenzene	Ethyl tert-butyl ether	1,1-Dichloroethene	Trichlorotrifluoroethane	Chloroethane	Chloroform
1,2-Dichloropropane	Isopropylbenzene	Methyl tert-butyl ether	Hexachlorobutadiene		Chloromethane	Dibromochloromethane
cis-1,3-Dichloropropene	Naphthalene		1,2,3-Trichlorobenzene		1,2-Dichlorobenzene	
trans-1,3-Dichloropropene	Styrene		Vinyl bromide		1,3-Dichlorobenzene	
Ethylene dibromide	Toluene		Vinyl chloride		1,1-Dichloroethane	
1,2,3-Trichloropropane	1,2,4-Trimethylbenzene		Bromochloromethane		1,2-Dichloroethane	
	o-Xylene		Carbon disulfide		cis-1,2-Dichloroethene	
	m- and p-Xylene		3-Chloropropene		trans-1,2-Dichloroethene	
	Xylenes (total)		trans-1,4-Dichloro-2-butene		Hexachloroethane	
	sec-Butylbenzene		1,3-Dichloropropane		Methylene chloride	
	tert-Butylbenzene		2,2-Dichloropropane		Perchloroethene	
	2-Ethyltoluene		1,1-Dichloropropene		n-Propylbenzene	
	p-Isopropyltoluene		Ethyl methacrylate		1,2,4-Trichlorobenzene	
	1,2,3,4-Tetramethylbenzene		Iodomethane		1,1,1-Trichloroethane	
	1,2,3,5-Tetramethylbenzene		Methyl acrylate		1,1,2-Trichloroethane	
	1,2,3-Trimethylbenzene		Methyl acrylonitrile		Trichloroethene	
	1,3,5-Trimethylbenzene		Methyl methacrylate		Acetone	
			Vinyl acetate		Bromobenzene	
					2-Chlorotoluene	
					4-Chlorotoluene	
					Dibromomethane	
					Diethyl ether	
					Methyl butyl ketone	
					Methyl ethyl ketone	
					Methyl isobutyl ketone	
					1,1,2,2-Tetrachloroethane	
					1,1,1,2-Tetrachloroethane	
					Tetrahydrofuran	

[1]This group does not reflect a predominant use of these compounds but instead represents a grouping based on origin and chemical class.

Table 2. Number of wells available for analysis in a national assessment of VOCs by data source and water use.

[NAWQA, National Water-Quality Assessment Program; --, no data]

Use of water	Data source				Total
	NAWQA aquifer studies	NAWQA shallow ground-water studies	Retrospective aquifer studies	National source-water survey	
	Number of wells				
Domestic	1,621	263	517	--	2,401
Public	321	8	192	575	1,096
Monitoring	136	--	199	--	335
Other	224	--	237	--	461
Unknown	11	--	40	--	51
Total	2,313	271	1,185	575	4,344

Aquifer studies were resource assessments designed to characterize the water quality of an aquifer used as a significant ground-water source throughout the Study Unit; no specific land-use type was targeted for sampling. The design for each aquifer study consisted of the selection of 20 to 30 wells for sampling in each network (Gilliom and others, 1995). The goal was to achieve a well density of approximately 1 well per 100 square kilometers (km^2). Wells were selected in an unbiased, random, spatially distributed manner throughout each study area. Aquifer systems sometimes were divided into subunits on the basis of physiographic and hydrogeologic features, and in some cases Study Units performed more than one aquifer study.

Existing wells, primarily domestic wells if available, were selected and sampled by NAWQA for aquifer studies. Domestic wells were chosen because of their random, spatially distributed locations. Also, existing wells were preferred over installation of new monitoring wells because of the high costs involved in installing wells. Each well in each aquifer study was initially sampled once, and this sample represented the primary environmental sample for the site. Data from a total of 2,313 wells in NAWQA aquifer studies were included in the national assessment of VOCs (table 2). NAWQA personnel collected these samples of ground water from these wells between 1993 and 2002.

Shallow ground-water studies were designed to assess the quality of ground water in the uppermost part of ground-water systems underlying a particular land use. The design for shallow ground-water studies beneath both urban and agricultural land-use areas consisted of the selection of 20 to 30 wells for sampling in each land-use setting (Gilliom and others, 1995). Typically, each Study Unit performed between 2 and 4 shallow ground-water studies. Shallow wells were designed to sample

recently recharged ground water less than 10 years old (Gilliom and others, 1995).

Like in aquifer studies, each well was initially sampled once in shallow ground-water studies. Wells were selected in an unbiased, random, spatially distributed manner throughout each land-use area. For studies in urban areas, most wells were installed by NAWQA and were located in areas where at least 75 percent of the land use within a 50m (meter) radius around the well was new residential/commercial land use (Squillace and Price, 1996). Data from 271 domestic or public wells in shallow ground-water studies were included in the national assessment of VOCs (table 2). NAWQA personnel collected these samples of ground water between 1993 and 1998.

Retrospective Data

Sampling of ground water by NAWQA for aquifer studies did not cover all areas of the United States. Consequently, existing data were sought to supplement NAWQA data. Some Federal, State, and local agencies have collected data on VOCs from aquifer studies with similar design characteristics and data-collection objectives as the NAWQA aquifer studies. The NAWQA Program compiled some of these data (hereafter referred to as "retrospective data") and included them in a national assessment of VOCs. The retrospective data are considered to be similar enough in design to data from the NAWQA aquifer studies to provide a broader national coverage.

Retrospective data were selected only if they met specific criteria, including monitoring objectives, study design, well construction, methods of sample collection, laboratory analysis, and quality control (Lapham and Tadayon, 1996). Details of the design of the retrospective data compilation

and the sampling and analytical criteria required for selection of retrospective data can be found in Lapham and Tadayon (1996). As of 2005, VOC data from more than 16,000 wells from about 50 ambient monitoring programs or studies have been compiled as part of the retrospective data. Data from a subset of 1,185 wells from the retrospective data met the selection criteria and were used in a national assessment of VOCs (table 2). These wells were sampled between 1985 and 1995.

Source-Water Data

In addition to NAWQA and retrospective data, data from another source were used to characterize the occurrence of VOCs in public well samples. Ground water used as a source of drinking water for community water systems (CWSs) was sampled in a national survey, hereafter referred to as the source-water survey. This survey was a collaborative effort between the American Water Works Association Research Foundation (AWWARF), the Metropolitan Water District of Southern California (MWDSC), the Oregon Health & Sciences University, participating CWSs, and the USGS. The purpose of this survey was to assess the occurrence, distribution, and magnitude of VOC contamination of source waters of CWSs, whether derived from surface water or ground water. Data from the source-water survey provided important insights into the quality of ground water used as source water for CWSs on a national scale.

The main focus of the source-water survey was determining the occurrence and distribution of the gasoline oxygenate methyl *tert*-butyl ether (MTBE) in source waters for CWSs. However, samples of source water also were analyzed for a suite of 65 other VOCs. Although samples of source water from surface water were analyzed in the source-water survey, only samples of source water from ground water were considered in a national assessment of VOCs.

With respect to ground water, two phases of the source-water survey were accomplished: (1) a random survey of 575 CWSs throughout the country, and (2) a focused survey of 80 CWSs throughout the country with suspected or known MTBE contamination (Clawges and others, 2001). Results of the random survey can be found in Grady (2003), and results of the focused survey can be found in Delzer and Ivahnenko (2003). Of the two phases of the source-water survey, only data from the random survey were used in the national assessment to avoid potential bias in the occurrence of VOCs.

The selection of CWSs for sampling in the random phase of the source-water survey was statistically based and stratified by population-served size category, source of water (ground water or surface water), and total number of people served (Ivahnenko and others, 2001). Personnel from CWSs collected samples between 1999 and 2000 from 575 public wells as part of the random phase of the source-water survey (table 2). Only one sample of ground water from one well in each CWS was analyzed. Samples of source water were analyzed by the MWDSC laboratory using USEPA approved method 524.2

(Grady, 2003). Additional details on the design of the random survey can be found in Ivahnenko and others (2001).

Field Sampling and Laboratory Analytical Methods

Most wells included in the national assessment of VOCs were sampled and analyzed by USGS personnel. This section presents a summary of USGS field and laboratory methods. More detailed information on USGS field and laboratory methodology is published elsewhere, and citations for these publications are included in subsequent parts of this section.

Each well sampled by NAWQA represents a distinct geographic site. The samples analyzed for this assessment represent the primary environmental sample or the first environmental sample collected from each well. Only one primary sample was included from each well because the goal of sampling was to provide a time snapshot of ground-water quality in aquifers without regard to temporal variations. Thus, the term sample is used here to indicate the results from a single well that represents a distinct geographic site.

For data not collected or analyzed by NAWQA, such as the retrospective data, careful selection procedures were used to ensure that these data had sufficient quality control for inclusion in the national assessment. For example, only retrospective data with VOC analyses performed by GC/MS in a laboratory certified by the USEPA were included in the national assessment. Details of the design of the retrospective compilation effort and of the sampling and analytical criteria required for selection of retrospective data have been published in Lapham and Tadayon (1996) and in Lapham, Neitzert, and others (1997). Field and laboratory methods used in the source-water survey are described by Koch and others (2003), and additional information is available at the Web site *http://water.usgs.gov/nawqa/vocs*.

Detailed guidelines and protocols have been developed by the USGS and NAWQA for the selection and installation of wells, documentation of wells, and collection of related data. These guidelines and protocols can be found in Lapham and others (1995) and Lapham, Wilde, and Koterba (1997). Subsequent descriptions of USGS field and laboratory methods include the following topics: (1) field sampling and handling, (2) laboratory analytical methods, (3) method used to analyze VOCs prior to April 1996, and (4) method used to analyze VOCs after April 1996.

Field Sampling and Handling

Protocols and procedures for the collection of water-quality data for the USGS and NAWQA Programs have been developed previously (Koterba and others, 1995; Wilde, Radtke, and others, 1999). These protocols and procedures were followed in collection of all ground-water samples by NAWQA. Ground-water samples were collected from the well before pressure tanks and water treatment, if any. Each

well was purged and field measurements were made before a sample of ground water was collected. A minimum volume of water, equal to three times the well casing volume, typically was purged. Towards the end of purging, the flow was reduced and pH, water temperature, specific conductance, and dissolved oxygen were monitored in a flow-through chamber. Sampling commenced only after sequential field measurements were within allowable differences. When used for sampling, submersible pumps were cleaned before a sample was collected. The cleaning procedure for pumps and other sampling equipment included an initial water flush with nonphosphate detergent, a deionized water rinse that was free of detectable concentrations of VOCs, a methanol rinse, and a final deionized water rinse.

Samples for VOC analyses were collected inside an environmental chamber designed to reduce potential airborne contamination. The flow of ground water to this chamber was reduced to about 200 milliliters (mL) per minute, and VOC samples were collected in standard 40mL amber glass vials. A preservative agent, 1:1 hydrochloric acid, was added to achieve a pH of approximately 2. After capping the vials, samples were checked for bubbles. Samples with bubbles were discarded and new samples were collected. Once preserved, bubble-free samples were placed in a cooler and kept at a temperature equal to or less than 4 degrees Celsius. These samples were then shipped to the USGS NWQL and nearly all samples were analyzed within 14 days of sample collection.

Laboratory Analytical Methods

All samples of ground water collected as part of the NAWQA Program were analyzed at the NWQL in Denver, Colorado. The NWQL analyzes thousands of natural waters samples each year from across the Nation. Ground-water samples are analyzed for many VOCs, and the analytical methodology for VOCs is similar to USEPA method 524 for drinking-water samples, although some operating conditions have been adjusted to optimize analytical performance. The NWQL has received approval by the USEPA and the State of Colorado for their methods of analyzing VOCs in water.

Nearly all of the ground-water samples collected by the NAWQA Program were analyzed for VOCs by purge and trap capillary column GC/MS (Rose and Schroeder, 1995; Connor and others, 1998). Mass spectrometry provides a reliable qualitative identification of each compound through its unique fragmentation pattern (Connor and others, 1998). Methods using this analytical technique were selected for use in the NAWQA Program because of the high degree of confidence in compound identification.

An exception to the use of GC/MS in analyses of VOCs in water is the determination of ethylene dibromide (EDB) and dibromochloropropane (DBCP). These two compounds have very low drinking-water standards compared to other VOCs, and the GC/MS method does not detect them at concentrations much less than these standards. In order to achieve a lower detection capability for DBCP and EDB, a different analytical

method (USGS method 0-3120-90) sometimes was used for these compounds. This method uses gas chromatography (GC) with an electron capture detector (ECD) instead of a mass spectrometer. The ECD is much more sensitive for halogenated compounds; however, it does not provide the same high degree of qualitative identification as the mass spectrometer. In the national assessment of VOCs, analytical results for DBCP and EDB by the GC/ECD method were selected, if available. Additional details on the analytical methodology for EDB and DBCP are available in Fishman (1993).

VOC Analyses Prior to April 1996

Except as described previously for EDB and DBCP, all of the ground-water samples collected in NAWQA studies prior to April 1996 were analyzed by USGS method 0-3127-94. The details of this method can be found in Rose and Schroeder (1995). This method was first used at the NWQL in 1988 and was developed to mimic USEPA method 524.2, revision 3. In the USGS method, VOCs are removed from a water sample by purging with helium and collected on a sorbent trap. The trap is then heated to desorb VOCs, which are separated by a Megabore gas chromatographic capillary column, and finally VOCs are determined by a full-scan quadrupole mass spectrometer. Compound identification is confirmed by both the GC retention time and by the resultant mass spectrum.

NAWQA's samples were analyzed by method 0-3127-94 through a request for schedule (SH) 2090 analysis. Schedule 2090 included qualification (identification), and quantitation of 59 analytes and the tentative identification of unknowns (other peaks that occurred on the GC). The minimum reporting level (MRL) for all but one of the 59 analytes was 0.2 microgram per liter (µg/L). In the method performance analysis, recoveries for the majority of VOCs ranged from 80 to 120 percent, with relative standard deviations of less than 10 percent (Rose and Schroeder, 1995).

It is noteworthy that all VOCs in SH 2090 analyses had MRLs of 0.2 µg/L, with the exception of DBCP, which had an MRL of 1.0 µg/L. Some qualified detections of VOCs at concentrations less than the reporting levels were evident to NWQL chemists. However, the reporting strategy for SH 2090 specified that concentrations less than the MRL be reported as "less than the MRL."

VOC Analyses after April 1996

An enhanced method for the analysis of VOCs in natural waters, method 0-4127-96, was implemented by the NWQL in April 1996. Details of the method are given in Connor and others (1998). The NAWQA Program accessed this method through a request for SH 2020. This method includes analyses of 86 VOCs and a tentative identification of unknowns. The enhanced VOC method also utilizes purge and trap, capillary column GC/MS. The major differences between the enhanced method and the VOC method prior to 1996 are (1) the inclusion of additional compounds and quality-control samples in the analysis; and (2) the implementation of a new reporting

convention that allows the reporting of qualified concentrations less than the MRLs of SH 2090.

The reporting of lower concentrations is facilitated by the use of bracketing blanks and other laboratory quality-control samples. The method also incorporates the use of the long-term method detection level (LT-MDL). The LT-MDL differs from a standard method detection limit (MDL) in that it accounts for the long-term variance of multiple instruments, multiple operators, and multiple calibrations over several months to a year (Connor and others, 1998).

To minimize the probability of false negatives, the laboratory reporting level is set by the NWQL at two times the LT-MDL (Oblinger Childress and others, 1999). A "<" remark is added to the concentration of the laboratory reporting level when a VOC fails the qualification criteria (Connor and others, 1998).

All VOCs included in the national assessment are included in this method. Additional compounds were added to this method by the NWQL to meet the needs of other USGS monitoring activities. All of the VOCs with Federal drinking-water standards and health advisories, as well as VOCs on USEPA's Candidate Contaminant List (U.S. Environmental Protection Agency, 2006), are included in this new method.

Details of the new reporting strategy used in method 0-4127-96 and approaches for analyzing data provided by this new method are given by Connor and others (1998) and Oblinger Childress and others (1999). Mass spectrometry used in this method provides enhanced identification. Qualitative identification of a compound is required before a concentration is reported. Compounds positively identified using mass spectrometry can be quantified even at concentrations less than the LT-MDL. Thus, in comparison to other analytical methods, method 0-4127-96 is classified as "information rich" by the NWQL (Oblinger Childress and others, 1999). Because lower concentrations of VOCs are reported by the new analytical method, it is hereafter referred to as the low-level analytical method.

An "E" remark code is added to VOC concentrations that are less than either the laboratory reporting level or the lowest calibration standard, whichever is higher, to indicate that the concentration is estimated by the NWQL. For information-rich methods, estimated concentrations have an increased, but unknown, risk of error in comparison to concentrations that are not estimated (Oblinger Childress and others, 1999).

An important procedure in method 0-4127-96 is the use of additional blanks to assess the daily instrument performance. Periodically, ground-water samples are bracketed with blanks. If a compound is not present in the bracketing blanks, the concentration in the ground-water sample is reported. However, if a compound is present in one or both of the bracketing blanks, a comparison is made between the concentrations. If the concentration of the compound in ground water is less than or equal to five times the largest bracketing blank, the compound concentration is reported as less than the laboratory reporting level. If the concentration of the compound in ground water is greater than five times the largest bracketing

blank, the compound concentration is reported as quantified or estimated.

Field and Laboratory Quality Assurance and Quality Control

This section outlines the quality-assurance (QA) protocols and quality-control (QC) procedures used in the national assessment of VOCs. The quality of the NAWQA occurrence information is ensured by several measures including, but not limited to, the following: documented instructions for the selection, installation, and characterization of wells sampled for VOCs (Lapham and others, 1995); written field and laboratory protocols and procedures for sampling and analysis; training of personnel; QC samples; participation in a blind sample program and multiple-laboratory performance evaluation studies; and by special studies to gain insights into analyte stability, contaminant carryover, and efficiency of protocols for equipment cleaning. Included in this section is information on (1) field QC samples, (2) laboratory QC samples, (3) the organic blind sampling project, and (4) laboratory certification.

Field Quality-Control Samples

Field QC samples are an essential and routine component of USGS field methods. The results of QC samples assist USGS hydrologists in interpreting the occurrence or lack of occurrence of specific contaminants in ground-water samples. Source solution blanks, equipment blanks, field blanks, replicate samples, and spike samples routinely are included in ground-water assessments. The specific purpose of each field QC sample, and the QA protocol associated with collecting the QC sample, have been described in detail elsewhere (Koterba and others, 1995; Wilde, Schertz, and Radtke, 1999).

Source solution blanks are used to determine the presence or absence of compounds in the water used to clean equipment and process field blanks. Equipment blanks evaluate the cleanliness of ground-water sampling equipment and typically are collected in a field office before ground-water sampling. Field blanks are collected near sampling wells and evaluate potential sample contamination from sampling equipment, cleaning procedures, and the atmosphere. Replicate samples of ground water measure the combined precision of sampling and laboratory analyses. Lastly, field matrix spiked samples primarily are used to assess stability of VOCs during shipment and storage prior to analysis. Field matrix spiked samples, when compared to laboratory reagent spiked samples, also can be used to determine matrix effects.

Results of field QC samples initially are reviewed by NAWQA Study Unit personnel. The Study Unit data then are aggregated to create a national data set for additional review and evaluation. An important objective of the latter review is to identify any systematic field contamination among Study Units. Such contamination is a rare occurrence. However, if

systematic field contamination is suspected, the environmental results associated with the systematic contamination are coded to indicate potential contamination and have been excluded from a national assessment of VOCs.

Laboratory Quality-Control Samples

Analyses by NWQL methods 0-3127-094 and 0-4127-96 include various types of laboratory QC samples as prescribed by the USEPA and others. These QC samples include instrument blanks, bracketing blanks (for method 0-4127-96 only), continuing calibration verification standards, set spikes, quality-control check standards, matrix-spiked samples, duplicate water samples, recovery of internal surrogate compounds, third-party check standards, and limit of quantitation standards (for method 0-4127-96 only). A more detailed review of the limit of quantitation standards (hereafter referred to as low-level spike samples) is given in the Assessment Levels section. Details on the purposes and procedures involved in these laboratory QC samples are beyond the scope of this report. Readers with an interest in this subject are referred to reports by Rose and Schroeder (1995) and Connor and others (1998).

The NWQL also participates in other quality-control activities including the Organic Blind Sample Project (OBSP) and laboratory certification. These activities are described briefly in the following sections.

Organic Blind Sample Project

The OBSP is conducted by USGS's Branch of Quality Systems and assesses the operational performance of organic analytical methods used to measure specific organic compounds in water samples. Assessments by the OBSP identify the baseline performance capabilities of the methods used in the NWQL's Organic Chemistry Program and are used to determine the strengths and weaknesses in the current system of bench-level quality and process control.

In the OBSP, blind samples of known chemical composition are randomly submitted to the NWQL for analysis. These samples are termed "blind" because the sample origin and analyte content are unknown to NWQL analysts. The blind samples are treated the same as ground- and surface-water samples through the entire NWQL process from login to data output. As such, blind samples reflect the performance of all the laboratory processes.

The analysis of VOCs by USGS methods 0-4127-96 and 0-3120-90 is included in the OBSP. All 55 VOCs included in the national assessment also are included in the OBSP. Results of the OBSP and additional background information on this program are posted at the Web site *http://bqs.usgs.gov*.

Laboratory Certification

The NWQL currently (2005) participates in the National Environmental Laboratory Accreditation Conference (NELAC) that certifies laboratories for the analysis of both potable and non-potable water samples. Specific analytes measured by specific agency methods are approved by the NELAC. The NELAC is administered by the New York State Department of Health and is supported by USEPA's National Environmental Laboratory Accreditation Program. The analysis of a large number of water constituents is approved through the NELAC. Analyses of 30 of the 55 VOCs included in the national assessment are approved by the NELAC using USGS analytical method 0-4127-96. The NELAC does not consider the other VOCs included in the national assessment for approval.

Prior to June 2004, the NWQL was certified by the USEPA for the analysis of VOCs in source- and drinking-water samples. However, this certification applied only to those VOCs with Maximum Contaminant Levels (MCLs) in drinking water as specified by the USEPA. The NWQL also has participated in numerous laboratory performance evaluation studies and laboratory audits. Discussion of these studies is beyond the scope of this report but results can be found at the Web site *http://nwql.usgs.gov*. The information is accessible from the "lab performance evaluation" menu at this Web site.

Computational and Statistical Methods

To characterize the quality of ground water and of samples from drinking-water supply wells, detection frequencies of VOCs were computed and VOC concentrations were compared to Federal drinking-water standards (MCLs) and to Health-Based Screening Levels (HBSLs). Statistical tests were performed to evaluate and compare data to better understand the anthropogenic and hydrologic processes associated with the occurrence of VOCs. This section outlines the computational and statistical methods used in the national assessment of VOCs. Included in this section is information on (1) detection frequencies and concentrations, (2) assessment levels, (3) statistical tests, and (4) comparisons of VOC concentrations to MCLs and HBSLs.

Detection Frequencies and Concentrations

The detection frequency of VOCs in ground water is an important indicator of water quality. Because NAWQA samples the quality of the ground-water resource, many of the concentration values are less than the practical sensitivity of the laboratory instruments and are reported as less than the reporting level. Factors that complicate the interpretation of detection frequencies include the variability of reporting levels among individual VOCs, the variability of reporting levels within individual VOCs, and the variability of reporting levels among data sets. Different data sets may have different laboratory reporting levels because they have different water-quality sampling objectives or analytical methods.

For both NAWQA and retrospective data, the reporting levels varied among individual VOCs. For NAWQA data, this variability was due to differences in instrument performance, resolution (which often is compound dependent), and/or laboratory conditions. In addition, many compounds have reporting levels that vary as method changes are implemented or new instrumentation is used (Oblinger Childress and others, 1999). For example, prior to April 1996, the default MRL used by the NWQL for most VOCs was 0.2 µg/L. Implementation of the low-level analytical method after this date resulted in substantially lower reporting levels for many compounds (Oblinger Childress and others, 1999). For retrospective data, the reporting levels also were quite variable among individual VOCs. This variability likely was due to the multiple laboratories that performed the analyses. Laboratories may use different laboratory censoring criteria and analytical methods and may have varying instrument sensitivities. Finally, sampling programs may have different water-quality assessment objectives that require varying reporting levels.

The detection frequency computed for a VOC is strongly dependent on the reporting level for the compound (Lapham and others, 2000). As a result, individual VOCs, groups of VOCs, and aquifer studies with varying reporting levels may produce detection frequencies that do not reflect true differences in water quality. Instead, they may simply represent differences in physical behavior of the VOC in the laboratory, laboratory instrument resolution, laboratory conditions, or simply the monitoring goals and objectives of the study.

Thus, for comparisons of detection frequencies among individual VOCs, among groups of VOCs, and among data sets with differing reporting levels, an assessment level was applied. An assessment level is a fixed concentration for computing detection frequencies of VOCs that have variable reporting levels. A detailed review of the assessment level concept and its application can be found in Lapham and others (2000). The assessments levels used for computing detection frequencies for the national assessment of VOCs are outlined in the next section.

Detection frequencies of VOCs were computed as follows:

One or more VOCs:

$$\frac{\textit{number of samples in which at least one VOC was detected at concentrations equal to or greater than the assessment level}}{\textit{total number of samples analyzed for the minimum number of VOCs}} \times 100$$

VOCs by group:

$$\frac{\textit{number of samples in which at least one VOC from a group was detected at concentrations equal to or greater than the assessment level}}{\textit{total number of samples analyzed for at least one VOC from a group}} \times 100$$

Individual VOCs:

$$\frac{\textit{number of samples in which an individual VOC was detected at concentrations equal to or greater than the assessment level}}{\textit{total number of samples analyzed for an individual VOC}} \times 100$$

Concentrations of VOCs also are an important indicator of water quality. Because both NAWQA and retrospective data have varying reporting levels, comparisons of detected VOC concentrations were performed at a uniform assessment level. This was necessary because the distribution of concentrations also is dependent on reporting levels. Thus, an assessment level was applied when concentrations were compared among individual VOCs or groups of VOCs.

Assessment Levels

Two tiers of assessments levels were used for computing detection frequencies of VOCs: (1) application of an assessment level of 0.2 µg/L, which represents the occurrence of VOCs at a historical NWQL Practical Quantitation Level (PQL); and (2) application of an assessment level of 0.02 µg/L, which represents the occurrence of VOCs using the new low-level analytical method of the NWQL. In all comparisons of concentrations in aquifer studies, an assessment level of 0.02 µg/L was applied because most quantified concentrations of VOCs were greater than or equal to this value. Comparisons at this assessment level were only applied to concentrations determined using the low-level analytical method.

In the first assessment-level tier, detection frequencies of one or more VOCs, groups of VOCs, and individual VOCs were computed using an assessment level of 0.2 µg/L, which is considered the PQL for the entire data set. The USEPA defines a PQL as the lowest concentration of a substance in ground waters that can be reliably determined within specified limits of precision and accuracy by 75 percent of the laboratories in a performance evaluation study (U.S. Environmental Protection Agency, 2004b). The PQL is an estimate of the practical sensitivity of an analytical methodology. The advantages of using a PQL approach in determining detection frequencies include (1) providing ease and clarity of understanding; (2) allowing for comparisons of detection frequencies between NAWQA and other data sets that have similar reporting levels of 0.2 µg/L; and (3) maximizing spatial coverage by including the largest number of wells.

Prior to April 1996, the NWQL had a default MRL of 0.2 µg/L for most VOCs (Rose and Schroeder, 1995). After that date, the laboratory adopted a new analytical approach that allowed for determinations of concentrations of most VOCs at or less than 0.2 µg/L (Oblinger Childress and others, 1999). Because the historical approach of the NWQL has been to determine the concentrations of most VOCs at or greater than 0.2 µg/L, this can be considered a PQL for all NAWQA-collected data. In addition, most reporting levels for VOC analyses in the retrospective data set are at or near 0.2 µg/L.

Finally, VOC data from the source-water survey, with one exception, had a uniform MRL of 0.2 µg/L. Thus, a level of 0.2 µg/L was considered the PQL for the entire data set and as a first tier assessment level for comparison of detection frequencies.

Applying an assessment level can result in several losses of information. First, information is lost because concentrations less than the assessment level are censored. In addition, to accurately compute detection frequency at a specific assessment level, laboratory reporting levels greater than the assessment level should be removed from the data set (Lapham and others, 2000). In the data set for the national assessment of VOCs, only a small percentage of analyses had laboratory reporting levels that exceeded 0.2 µg/L. These higher laboratory reporting levels were included in the computations of detection frequencies at the first tier assessment level because of their minimal occurrence in the data set and because their inclusion did not significantly affect detection frequencies.

Because the laboratory reporting level for DBCP was greater than 0.2 µg/L in many cases, the detection frequency of DBCP may be substantially underestimated at an assessment level of 0.2 µg/L. Although acrolein and acrylonitrile also had laboratory reporting levels that were consistently greater than 0.2 µg/L, these two compounds were never detected. Acrolein was removed from the analytical schedule on April 30, 1998, due to poor performance with a new purge and trap concentrator.

For the second assessment-level tier, detection frequencies of one or more VOCs, groups of VOCs, and individual VOCs were computed using an assessment level of 0.02 µg/L. In computing detection frequencies at this assessment level, only a subset of wells from the data set was used. Because only samples analyzed after April 1, 1996, had the new low-level analytical method, only data from NAWQA Study Units that began high-intensity work in 1994 or 1997 were used for the second tier assessment level. In general, these Study Units collected samples after April 1, 1996. However, one exception to this occurred. The Central Nebraska (CNBR) Study Unit began high-intensity work prior to 1994, but samples from 27 wells from this Study Unit were not collected until after implementation of the new low-level analytical method. These data were not included in detection frequency computations at assessment level of 0.02 µg/L because there were few detections at concentrations less than 0.2 µg/L in these well samples. However, samples from these 27 wells were included in the detection frequency computations at an assessment level of 0.2 µg/L.

The confidence associated with computed detection frequencies at 0.02 µg/L was dependent on the LT-MDL of the compound and the fraction of concentrations less than 0.05 µg/L. The LT-MDL is related to the MDL. The MDL is described as the minimum concentration of a substance that can be measured and reported with 99-percent confidence that the analyte concentration is greater than zero (U.S. Environmental Protection Agency, 2003b). The MDL is determined from analyses of seven or more samples that contain the ana-

lyte. The LT-MDL is used by the NWQL and also is described as the minimum concentration of a substance that can be measured and reported with 99-percent confidence. However, the LT-MDL is derived from the standard deviation of a minimum of 24 spike sample measurements over an extended period of time (Oblinger Childress and others, 1999). The LT-MDL data are collected at the NWQL on a continuous basis and are examined periodically to assess year-to-year variations. If necessary, the LT-MDL of certain compounds is adjusted in accordance with the response of the analytical instruments.

If the LT-MDL of a VOC was consistently greater than 0.02 µg/L and the VOC had few detections at concentrations less than 0.05 µg/L, detection frequencies computed for that VOC at an assessment level of 0.02 µg/L could substantially underestimate the true detection frequency of the VOC in the environment. Consequently, all detection frequencies computed at an assessment level of 0.02 µg/L are considered to be estimated and are indicated as such.

In establishing laboratory reporting levels for VOCs using the low-level analytical method, the NWQL has set an acceptable risk of false positives and false negatives of no more than 1 percent each. False positives are indications that a VOC may be present in a sample when it is not present. False positives are detrimental to environmental analytical information because they can overstate the true environmental presence of the VOC in ground water. At the LT-MDL concentration, the chance of a false positive is limited to less than or equal to 1 percent through a variety of laboratory quality-control evaluations (Connor and others, 1998). However, at concentrations less than the LT-MDL, the risk of false positives can increase rapidly (Oblinger Childress and others, 1999).

Because of the information-rich methods used by the NWQL, concentrations of VOCs can be reported when less than the LT-MDL. Although this reporting strategy can increase the risk of false positives, the NWQL uses various analytical strategies to reduce this risk. For example, before a compound is reported as present in a sample, it must pass rigorous qualification criteria including correct elution time from the gas chromatograph and the correct fragmentation ions and ion ratios from the mass spectrometer. These criteria ensure that the compound is present in the sample (Connor and others, 1998).

In addition, the NWQL analyzes bracketing blanks to limit the likelihood of false positives at low concentrations. Bracketing blanks are analyzed before and after every set of environmental samples. The results of the environmental samples are compared to the bracketing blanks. Quantified concentrations in environmental samples are reported only if the concentration of the compound in the environmental sample is greater than five times the highest bracketing blank concentration (Connor and others, 1998).

False negatives are indications that a VOC may not be present in a sample when it is present. False negatives are detrimental to environmental analytical information because they can understate the true environmental presence of the VOC in ground water. At the LT-MDL concentration, the chance of

false negatives is 50 percent. In order to limit the chance of false negatives to less than or equal to 1 percent, the laboratory reporting level for each VOC reported on schedule SH 2020 is set at two times the LT-MDL (Oblinger Childress and others, 1999). Therefore, if an assessment level is applied that is equal to the LT-MDL of a compound, the chance of false negatives when computing a detection frequency for that compound is 50 percent. In this case, the detection frequencies computed for that compound may underestimate the true occurrence of the compound in the environment.

Because of the qualification criteria (for example elution time, fragmentation ions, ion ratios, and bracketing blanks) used by the laboratory, all reported concentrations including those less than the LT-MDL, are assumed to indicate the valid presence of the compound in the environmental sample even though the concentrations may be estimations. However, if the assessment level is less than the LT-MDL of a compound, an additional increase in the risk of false negatives beyond 50 percent may occur when computing a detection frequency. The precise risk of false negatives in this scenario is not known but it is assumed that the risk of false negatives is greater than 50 percent (Oblinger Childress and others, 1999).

Low-level spike samples (also known as limit of quantitation standards) are analyzed routinely at the NWQL at concentrations near the LT-MDL of each compound in order to check analytical performance at low concentrations and limit the likelihood of false negatives. The results of VOC spike sample tests from November 2002 to September 2003 characterized the performance of the low-level method and indicate that instrument performance for most compounds was good at concentrations near the LT-MDL with 100 percent identification of nearly all spiked VOCs (table 3). The recovered concentrations from the low-level spike samples all had relative standard deviations less than 25 percent (table 3). Because most VOCs were spiked at or near a concentration of 0.05 µg/L, instrument performance for all compounds at this level was considered good and the risk of false negatives was assumed to be minimal.

The LT-MDLs for individual VOCs vary through time for NAWQA data analyzed with the low-level analytical method. Variability in LT-MDLs also exists among individual VOCs. The median LT-MDLs for each of the 55 VOCs included in the national assessment of VOCs are listed in table 3. These values were determined from NWQL laboratory QC analyses performed during 1997–2003. The median LT-MDLs varied by more than one order of magnitude among compounds, and many of the compounds have median LT-MDLs that are greater than the second-tier assessment level of 0.02 µg/L. Because of this variability, it was necessary to further understand the effect of false negatives on the confidence associated with computations of detection frequencies at an assessment level of 0.02 µg/L. If the likelihood of false negatives is high for a compound with a median LT-MDL greater than 0.02 µg/L, the computed detection frequency may underestimate the true environmental occurrence of that compound at the second tier assessment level of 0.02 µg/L.

Figure 2 shows the estimated rate of false negatives for each VOC based on the median LT-MDL of the compound relative to an assessment level of 0.02 µg/L. The estimated likelihood of false negatives for each compound also is presented in table 3. No VOC had an estimated rate of false negatives less than 1 percent. This is because no VOC had a median LT-MDL that was less than one-half the assessment level of 0.02 µg/L (for example < 0.01 µg/L).

Twenty-one VOCs, including two VOCs that were never detected at an assessment level of 0.02 µg/L (*cis*-1,3-dichloropropene and ethlyene dibromide) , had median LT-MDLs less than or equal to 0.025 µg/L, which is less than or equal to the second tier assessment level of 0.02 µg/L using two significant figures. As such, these VOCs were identified as those for which a computed detection frequency would have a likelihood of false negatives of less than or equal to 50 percent and thus a high confidence of not underestimating the true environmental occurrence (table 3). These VOCs are identified as Group 1 compounds (fig. 3). Only nineteen Group 1 compounds were detected relatively frequently, four were detected infrequently (table 3).

The remainder of VOCs had median LT-MDLs that were greater than 0.025 µg/L. These VOCs were placed into two additional groups based on the fraction of detections with concentrations less than or equal to 0.05 µg/L. Because the majority of low-level spike sample concentrations were about 0.05 µg/L (table 3), this level was chosen as a criterion for determining if a compound had low-concentration analytical capability. The groups represent the estimated likelihood of false negatives associated with each and the confidence that the detection frequencies are not underestimated at an assessment level of 0.02 µg/L.

Group 2 compounds are VOCs with median LT-MDLs greater than 0.025 µg/L and with 50 percent or more of all detections with concentrations less than or equal to 0.05 µg/L (fig. 3). A value of 20 or more detections was selected as a minimum so that the fraction of concentrations value would be meaningful. Seven compounds are in this group, with *m*- and *p*-xylene considered as two compounds even though they can not be separated analytically (table 3). Although the median LT-MDLs of compounds in this group are greater than 0.025 µg/L, the likelihood of false negatives is assumed to be low because of the high percentage of detections with concentrations less than or equal to 0.05 µg/L. For example, toluene has a LT-MDL greater than 0.025 µg/L suggesting a high rate of false negatives (fig. 2); however, more than 50 percent of detections of toluene were less than or equal to 0.05 µg/L indicating good low-level analytical resolution for this compound and thus a reduced risk of false negatives. Because the likelihood of false negatives is believed to be low for Group 2 compounds, confidence is high that detection frequencies computed at 0.02 µg/L do not underestimate the true environmental occurrence.

Table 3. Median long-term method detection level, and percent of detections less than or equal to 0.05 microgram per liter for volatile organic compounds in ground water, data on spiked concentrations and recoveries, and confidence of detection frequency computations.

[LT-MDL, long-term method detection limit; RSD, relative standard deviation; µg/L, microgram per liter; ≤, less than or equal to; <, less than; ≥, greater than or equal to; --, no data; see figure 3 for explanations of groups]

Compound	Median LT-MDL (µg/L)	Percent of detections ≤0.05 µg/L	Total number of detections in ground water at an assessment level of 0.02 µg/L (number of samples)	Spiked concentration for analytical performance (µg/L)	Detection frequency of spike samples[1] (percent)	Mean recovery from spike samples[1] (percent)	RSD of recovered concentrations[1] (percent)	Estimated likelihood of false negatives at 0.02 µg/L[2]	Confidence that the computed detection frequency is NOT underestimated
			Detected relatively frequently in ground water at an assessment level of 0.02 µg/L (>1 percent)						
			Group 1						
Benzene	0.0245	88	69 (1,687)	0.05	100	109	8.2	Low	High
Bromodichloromethane	.024	52	82 (1,686)	.05	100	108	12	Low	High
Chlorobenzene	.014	82	22 (1,687)	.05	100	100	11	Low	High
Chloroform	.019	58	503 (1,686)	.05	100	107	12	Low	High
1,4-Dichlorobenzene	.025	84	43 (1,687)	.05	100	104	16	Low	High
1,1-Dichloroethene	.021	70	37 (1,686)	.05	100	103	10	Low	High
cis-1,2-Dichloroethene	.019	55	38 (1,686)	.05	100	103	9.8	Low	High
1,2-Dichloropropane	.0245	32	22 (1,686)	.07	00	106	8.4	Low	High
Ethylbenzene	.015	71	14 (1,687)	.05	100	97	15	Low	High
Isopropylbenzene	.0175	82	17 (1,687)	.05	100	97	17	Low	High
Styrene	.021	92	38 (1,665)	.016	100	111	22	Low	High
Trichloroethene	.019	52	88 (1,686)	.05	100	102	7.6	Low	High
1,1,1-Trichloroethane	.016	70	138 (1,687)	.05	100	101	11	Low	High
Trichlorotrifluoroethane	.0245	47	17 (1,686)	.05	100	101	15	Low	High
o-Xylene	.019	66	17 (1,682)	.06	100	101	13	Low	High
			Group 2						
Carbon tetrachloride	0.03	55	22 (1,686)	0.09	100	97	16	Low	High
1,1-Dichloroethane	.026	54	48 (1,686)	.07	100	102	10	Low	High
Perchloroethene	.038	60	219 (1,656)	.11	100	107	13	Low	High
Toluene	.03	71	275 (1,676)	.05	100	105	9.9	Low	High
1,2,4-Trimethylbenzene	.028	74	266 (1,662)	.06	100	99	17	Low	High
m- and p-Xylene[3]	.031	79	42 (1,683)	.12	100	92	15	Low	High

Table 3. Median long-term method detection level, and percent of detections less than or equal to 0.05 microgram per liter for volatile organic compounds in ground water, data on spiked concentrations and recoveries, and confidence of detection frequency computations.—Continued

Compound	Median LT-MDL (µg/L)	Percent of detections ≤0.05 µg/L	Total number of detections in ground water at an assessment level of 0.02 µg/L (number of samples)	Spiked concentration for analytical performance (µg/L)	Detection frequency of spike samples[1] (percent)	Mean recovery from spike samples[1] (percent)	RSD of recovered concentrations[1] (percent)	Estimated likelihood of false negatives at 0.02 µg/L[2]	Confidence that the computed detection frequency is NOT underestimated
				Group 3					
Bromoform	0.05	46	37 (1,685)	0.2	100	102	15	High	Low
Chloromethane[4]	.12	81	132 (1,676)	.3	100	103	21	High	Low
Dibromochloromethane	.091	36	33 (1,686)	.18	100	103	13	High	Low
Dichlorodifluoromethane	.08	11	70 (1,687)	.5	100	97	24	High	Low
Methyl *tert*-butyl ether	.08	12	119 (1,687)	.2	100	99	9.5	High	Low
Methylene chloride	.14	36	33 (1,686)	.18	100	101	9.6	High	Low
Trichlorofluoromethane	.048	44	41 (1,686)	.2	100	101	17	High	Low
1,2,3-Trichloropropane	.08	0	10 (1,687)	.3	100	98	12	High	Low
Detected relatively infrequently in ground water at an assessment level of 0.02 µg/L (< 1 percent)									
				Group 1					
1,2-Dichlorobenzene	0.024	67	9 (1,687)	0.05	100	110	14	Low	High
1,3-Dichlorobenzene	.021	86	7 (1,687)	.05	100	106	15	Low	High
trans-1,2-Dichloroethene	.016	100	5 (1,686)	.05	100	102	8.1	Low	High
n-Propylbenzene	.021	60	5 (1,687)	.05	100	97	19	Low	High
				Group 3					
tert-Amyl methyl ether	0.056	27	11 (1,683)	0.11	100	95	11	High	Low
n-Butylbenzene	.092	67	3 (1,687)	.19	100	89	16	High	Low
Choroethane	.06	60	5 (1,686)	.12	100	103	15	High	Low
Dibromochloropropane	.11	0	3 (1,687)	.5	100	96	15	High	Low
1,2-Dichloroethane	.069	0	3 (1,687)	.21	100	109	13	High	Low
Diisopropyl ether	.05	22	9 (1,547)	.1	100	98	11	High	Low
Ethyl *tert*-butyl ether	.027	100	3 (1,683)	.05	100	99	12	High	Low
Hexachlorobutadiene	.07	100	1 (1,687)	.14	100	108	19	High	Low

Table 3.   Median long-term method detection level, and percent of detections less than or equal to 0.05 microgram per liter for volatile organic compounds in ground water, data on spiked concentrations and recoveries, and confidence of detection frequency computations.—Continued

Compound	Median LT-MDL (µg/L)	Percent of detections ≤0.05 µg/L	Total number of detections in ground water at an assessment level of 0.02 µg/L (number of samples)	Spiked concentration for analytical performance (µg/L)	Detection frequency of spike samples[1] (percent)	Mean recovery from spike samples[1] (percent)	RSD of recovered concentrations[1] (percent)	Estimated likelihood of false negatives at 0.02 µg/L[2]	Confidence that the computed detection frequency is NOT underestimated
					Group 3—Continued				
Naphthalene	.13	0	5 (1,687)	.5	99.4	86	15	High	Low
1,2,3-Trichlorobenzene	.14	100	1 (1,687)	.27	100	98	15	High	Low
1,2,4-Trichlorobenzene	0.09	100	1 (1,687)	0.19	100	95	15	High	Low
1,1,2-Trichloroethane	.032	100	3 (1,687)	.06	100	110	11	High	Low
Vinyl chloride	.056	0	2 (1,687)	.11	97.1	107	13	High	Low
					Not detected				
Acrolein[5]	--	0	0 (618)	--	100	--	--	High	Low
Acrylonitrile	0.6	0	0 (1,683)	2.4	100	106	8.4	High	Low
Bromomethane	.10	0	0 (1,687)	.5	97.1	87	20	High	Low
cis-1,3-Dichloropropene	.02	0	0 (1,687)	.09	100	101	12	Low	High
trans-1,3-Dichloropropene	.04	0	0 (1,686)	.13	100	104	12	High	Low
Ethylene dibromide	.018	0	0 (1,686)	.05	100	102	9.7	Low	High
Hexachloroethane	.07	0	0 (1,683)	.19	100	102	17	High	Low
Vinyl bromide	.05	0	0 (1,683)	.2	100	97	13	High	Low

[1] Analyzed from November 2002 to September 2003.

[2] Low indicates a rate of false negatives ≤50 percent, whereas high indicates a rate of false negatives >50 percent.

[3] m- and p-Xylene are considered as two compounds.

[4] In group 3 because of poor lab performance.

[5] Removed from the analytical schedule after April 30, 1998; prior to this date the median LT-MDL was 1.43 µg/L.
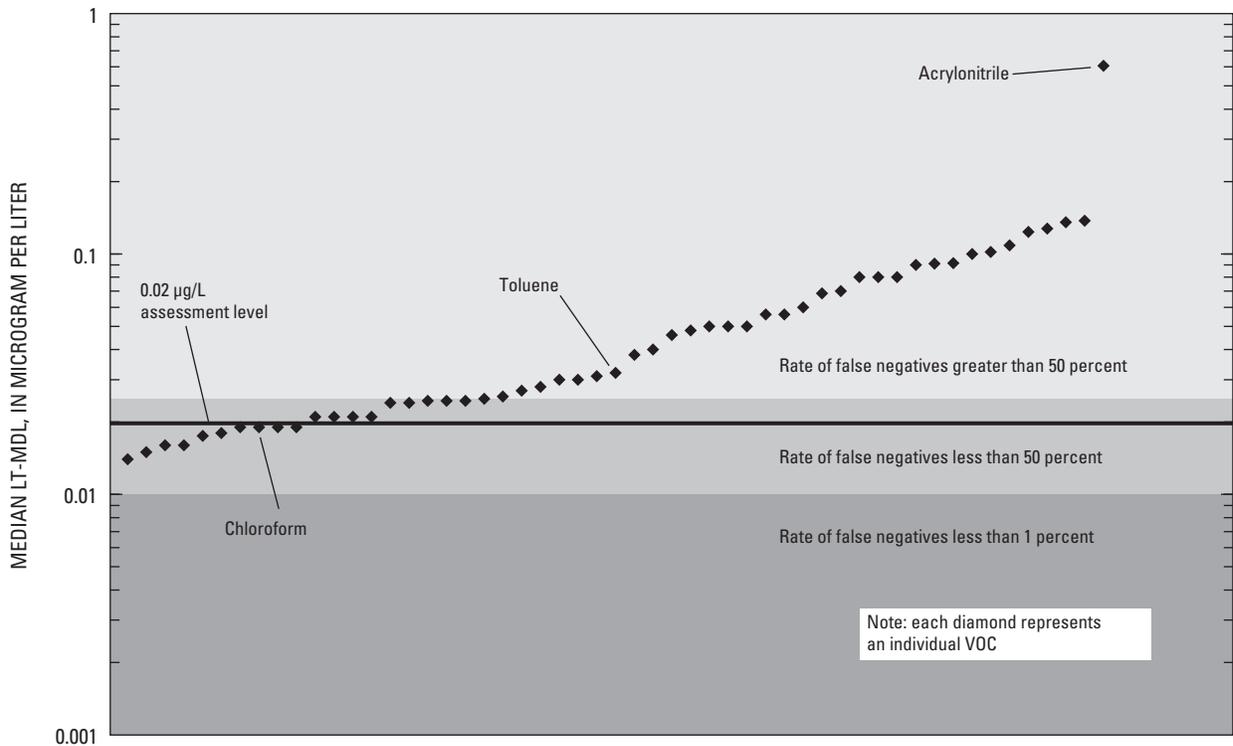
Figure 2.   Median long-term method detection level (LT-MDL) for each volatile organic compound (VOC) and the estimated rate of false negatives when using an assessment level of 0.02 microgram per liter.
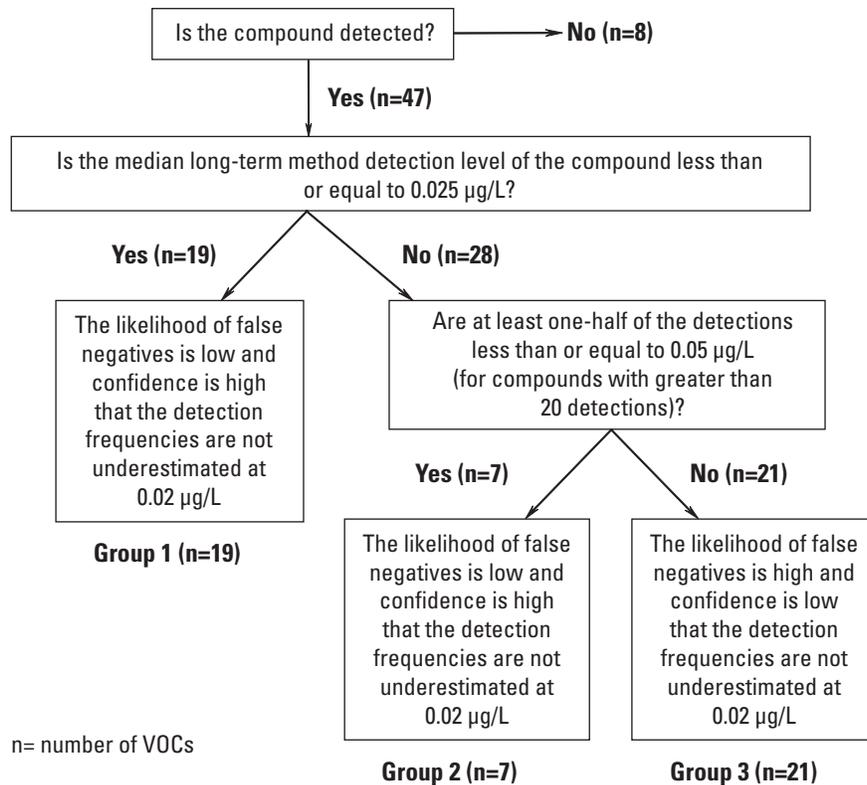
Figure 3.   Flow chart showing decisions for placing each volatile organic compound (VOC) into a group reflecting confidence of detection frequencies when using an assessment level of 0.02 microgram per liter (µg/L).

Group 3 compounds are VOCs with LT-MDLs greater than 0.025 µg/L and with either less than 20 detections or less than 50 percent of all detections with concentrations less than or equal to 0.05 µg/L. There are 21 VOCs in this group (table 3). The likelihood of false negatives is assumed to be high because the median LT-MDLs of VOCs in this group are greater than 0.025 µg/L and because these VOCs have a low percentage of detections with concentrations less than or equal to 0.05 µg/L. Because the likelihood of false negatives may be high for these VOCs, confidence is low that detection frequencies computed at 0.02 µg/L do not underestimate the true environmental occurrence. Although chloromethane did not meet the specific criteria, it was placed in group 3 because of its erratic laboratory performance.

Statistical Tests

A variety of statistical tests were performed to better explore the results. Nonparametric statistical tests were used for all analyses because the data were not assumed to have any particular distribution. Detailed information on the statistical tests used can be found in Helsel and Hirsch (1993). For all statistical tests, the selected significance level (α) was 0.05.

In the case of two or more categorical variables, a Pearsons chi-square test of independence, with Yates continuity correction, was performed. Yates continuity correction was used for a conservative test of significance. The null hypothesis of this test states that the distribution of data among the categories of one or more variables is not affected by the classification of one or more other variables. An example would be a comparison of the detection frequencies of chloroform between two or more aquifer studies. If the null hypothesis is rejected, the detection frequency of chloroform is dependent on the aquifer study.

In the case of two independent groups of continuous data, a Wilcoxon rank-sum test, or Mann-Whitney test, was performed. In its general form, the null hypothesis of this test states that observations from one group tend to produce larger values compared to another group. An example of this would be a comparison of concentrations of trichloroethene between two aquifer studies. If the null hypothesis is rejected, then the concentration of trichoroethene is higher in one study compared to another.

In the case of matched pairs of continuous data, a Wilcoxon signed-rank test was performed. The null hypothesis of this test states that the median difference between paired observations equals zero. An example of this would be a comparison of detection frequencies of VOCs by group between two aquifer studies. The detection frequency of one VOC group in one study compared to another study represents one matched pair. If the null hypothesis is rejected, then the detection frequencies of VOCs by group between the two studies are different.

In order to determine a relation between two continuous variables, a Spearman correlation test was performed. This test measures the strength of a monotonic relation between the two variables. The null hypothesis states that the test statistic, rho, is equal to zero. An example of this would be a test of the correlation between the concentrations of toluene in one aquifer study compared to another. If the null hypothesis is rejected, then there is a correlation between the concentrations of toluene in one aquifer study compared to another aquifer study. For sample sizes less than 20, Kendalls tau test was performed to measure the strength of a monotonic relation between two variables. The null hypothesis for this test is the same as for the Spearman correlation test.

To test the statistical significance of distributional differences, the nonparametric Kolmogorov-Smirnov test was used. The null hypothesis states that the distributions are not significantly different. If the null hypothesis is rejected, the distributions are considered significantly different. For example, if the distributions of concentrations are significantly different, the concentrations of one distribution are higher or lower than the other.

For determining associations between multiple explanatory variables and the probability of detecting individual VOCs, multivariate logistic regression analyses were used. The regression results only were used to determine associations between individual VOC occurrence and explanatory variables and to determine the strength and direction of the associations; the results were not used for predictive purposes. Explanatory variables were selected that could provide general insight or understanding into the sources, transport processes, or environmental mechanisms that influence or affect VOC contamination.

The magnitude and sign of the estimated slope coefficient in the logistic regression equation determines the strength and direction of the association of an explanatory variable with the probability of detecting VOCs according to the following equation:

$$ P = \frac{e^{(\beta_0 + \beta_1 X_1 + \ldots \beta_i X_i)}}{1 + e^{(\beta_0 + \beta_1 X_1 + \ldots \beta_i X_i)}} $$

where

P = probability of detecting an individual VOC,
β_0 = the y-intercept,
β_i = slope coefficient of X_i explanatory variables, and
X_i = 1 to i explanatory variables.

Estimated slope coefficients with positive signs indicate an increase in the probability of detecting VOCs with an increase in the explanatory variable, whereas estimated coefficients with negative signs indicate a decrease in the probability of detecting VOCs with an increase in the explanatory variable. However, the estimated slope coefficients do not give an accurate assessment of the strength of the association between explanatory variables because the units of each variable, especially continuous variables, have large differences in magnitude and variance. Therefore, standardized coefficients were computed in order to compare the slope coefficients between variables. The standardized coefficients indicate how

many standard deviations of change in the dependent variable are associated with one standard deviation of change in the explanatory variable (Menard, 2002).

Explanatory variables were entered into the logistic regression manually in a step-wise manner, and the regression was analyzed for significance at each step. For the overall regression, if the likelihood ratio of the model produced a p-value of <0.05, all explanatory variables were considered significantly associated with the probability of detecting VOCs. The significance of nested logistic regression models was tested using the partial likelihood ratio test. For cases where one additional coefficient was added, the Wald statistic was used to determine significance of the added coefficient. If the Wald statistic p-value of the slope coefficient was less than 0.05, and the upper and lower bounds of the odds ratio did not include 1, the additional variable was considered significantly associated with the probability of detecting VOCs. The significance of non-nested regression analyses was tested using Akaikes Information Criteria (Helsel and Hirsch, 1993).

Comparisons of VOC Concentrations to Drinking-Water Standards and Health-Based Screening Levels

Human-health standards are designed to protect public health by limiting the levels of contaminants in drinking water. To communicate the relevance of the water-quality findings in a human-health context, VOC concentrations in samples from domestic and public wells were compared to MCLs for regulated compounds and to HBSLs for unregulated compounds (Toccalino and others, 2003). As used in this report, a regulated compound is a compound for which a Federal drinking-water standard (usually an MCL) has been established by the USEPA. In general, samples for the national assessment of VOCs were collected prior to any type of treatment or distribution of the water. Thus, these results from them do not indicate a direct risk to human health. However, in one selected survey, VOC concentrations were analyzed in drinking water samples from CWSs and provide a more direct measure of risk to human health.

An MCL is a legally enforceable standard that sets the maximum permissible level of a contaminant in water that is delivered to any user of a public water system. Public water systems that allow distribution of drinking water with concentrations of water-borne constituents greater than MCLs are subject to fines and possible legal actions. Federal MCLs set limits in drinking water for 29 of the 55 VOCs included in a national assessment of VOCs. Some State health agencies have established MCLs that are enforceable only in public water supplies in that State. State MCLs were not considered in a national assessment of VOCs.

HBSLs are estimates of benchmark concentrations of contaminants that may be of potential human-health concern. HBSLs were developed collaboratively by the USGS, USEPA, New Jersey Department of Environmental Protec-

tion, and Oregon Health & Science University. HBSLs were calculated for 15 of the 26 unregulated compounds included in a national assessment of VOCs. HBSLs were not calculated for the remaining 11 VOCs due to a lack of toxicity information. Although HBSLs are not regulatory standards and are not legally enforceable, they can provide valuable information concerning water quality with respect to human health for contaminants that previously had no existing human-health standards or when only information on human-health implications are sought (Toccalino and others, 2003).

Table 4 lists applicable MCLs and HBSLs for 55 VOCs included in a national assessment of VOCs. Both MCLs and HBSLs were developed for individual VOCs with several exceptions. The four THMs bromodichloromethane, bromoform, chloroform, and dibromochloromethane have a combined MCL of 80 µg/L and are regulated on the basis of the sum of concentrations of these four compounds in a sample. Similarly, the three xylene isomers m-xylene, o-xylene, and p-xylene have a combined MCL concentration of 10,000 µg/L.

Only MCLs and HBSLs were compared to VOC concentrations. If the HBSL for a VOC was a range, the lower end of the range was used for comparison. No assessment level was applied when comparing concentrations to MCLs or HBSLs. Concentrations of VOCs within one order of magnitude of MCLs and HBSLs also were summarized.

VOC and Ancillary Data Sets

This section provides detailed information on the VOC and ancillary data sets used in the national assessment of VOCs. Included in this section is information on (1) the VOC data set used in the assessment of ground water; (2) the VOC data set used in the assessment of drinking-water supply wells; (3) the VOC data set used in the comparisons to drinking-water quality; (4) the VOC data set used in the relational analyses; (5) the ancillary data used in the relational analyses; and (6) other ancillary data.

VOC Data Used in Assessment of Ground Water

To determine the occurrence of VOCs in ground water, two sources of data were used (1) data from the NAWQA Program, which sampled aquifers throughout the United States during 1993–2002; and (2) retrospective data compiled from Federal, State, and local agencies that sampled aquifers during 1985–1997. Information on the design and implementation of data collection for the NAWQA Program was described previously. Detailed information on the assessment plan, data compiled, and the characteristics of the retrospective data can be found in Lapham and Tadayon (1996), Lapham, Neitzert, and others (1997), and Lapham and others (2000). Retrospective data were compiled from agencies that conducted ground-water monitoring in studies similar to the NAWQA aquifer studies.

Table 4.   Maximum Contaminant Levels (MCLs) and Health-Based Screening Levels (HBSLs) for the 55 volatile organic compounds included in the national assessment.

[µg/L, micrograms per liter; --, not available or not reported]

Compound	MCL (µg/L)	HBSL (µg/L)	Compound	MCL (µg/L)	HBSL (µg/L)
Fumigants			**Refrigerants**		
Bromomethane	--	100	Dichlorodifluoromethane	--	1,000
Dibromochloropropane	0.2	--	Trichlorofluoromethane	--	2,000
1,4-Dichlorobenzene	75	--	Trichlorotrifluoroethane	--	200,000
1,2-Dichloropropane	5	--	**Solvents**		
cis-1,3-Dichloropropene	--	[1].3	Carbon tetrachloride	5	--
trans-1,3-Dichloropropene	--	[1].3	Chlorobenzene	100	--
Ethlyene dibromide	0.05	--	Chloroethane	--	--
1,2,3-Trichloropropane		40	Chloromethane	--	30
Gasoline hydrocarbons			1,2-Dichlorobenzene	600	--
Benzene	5	--	1,3-Dichlorobenzene	--	600
n-Butylbenzene	--	--	1,1-Dichloroethane	--	--
Ethylbenzene	700	--	1,2-Dichloroethane	5	--
Isopropylbenzene	--	700	cis-1,2-Dichloroethene	70	--
Naphthalene	--	100	trans-1,2-Dichloroethene	100	--
Styrene	100	--	Hexachloroethane	--	.7
Toluene	1,000	--	Methylene chloride	5	--
1,2,4-Trimethylbenzene	--	--	Perchloroethene	5	--
o-Xylene	[2]10,000	--	n-Propylbenzene	--	--
m- and p-Xylene	[2]10,000	--	1,2,4-Trichlorobenzene	70	--
Gasoline oxygenates			1,1,1-Trichoroethane	200	--
tert-Amyl methyl ether	--	--	1,1,2-Trichoroethane	5	--
Diisopropyl ether	--	--	Trichloroethene	5	--
Ethyl tert-butyl ether	--	--	**Trihalomethanes**		
Methyl tert-butyl ether	--	--	Bromodichloromethane	[4]80	--
Organic synthesis			Bromoform	[4]80	--
Acrolein	--	4	Chloroform	[4]80	--
Acrylonitrile	--	[3]0.06-6	Dibromochloromethane	[4]80	--
1,1-Dichloroethene	7	--			
Hexachlorobutadiene	--	1			
1,2,3-Trichlorobenzene	--	--			
Vinyl bromide	--	--			
Vinyl chloride	2	--			

[1]Value is for total 1,3-dichloropropene isomers (*cis*- and *trans*-1,3-dichloropropene).

[2]Value is for total xylenes (*o*-, *m*-, and *p*-xylene).

[3]The HBSL is a range. The lowest value of this range was used for comparison to environmental concentrations.

[4]Value is for total trihalomethanes.

Various criteria were used to select data used in an assessment of VOCs in ground water. The selection criteria included the study type, number of wells in the study, the intended purpose of the sample, the number of VOCs analyzed, laboratory reporting levels, and distance between wells. The criteria were selected and applied to ensure that data for assessing the occurrence of VOCs in ground water were uniform and unbiased.

Only wells in NAWQA studies that were designed to survey water quality in aquifers were included in the data set. Wells in other types of studies were not included. Studies not included in the data set either targeted a specific land-use setting or had sampling objectives that were narrower than those for the general assessment of VOCs in ground water. Samples from springs were collected in some NAWQA aquifer studies. However, data from spring samples were excluded because it is known that the quality of ground water derived from springs differs from the quality of ground water derived from wells.

An aquifer study was required to have samples from at least 10 wells to be included in the data set. This was required because computing detection frequencies for studies with less than 10 wells can result in inaccurate, highly variable detection frequency values. These can skew or bias the detection frequency distribution. In some cases, studies that had a small number of wells were aggregated to form larger studies if the design and collection of all the smaller studies were similar and if they all represented an assessment of VOCs in a single aquifer. If a single well was used in more than one study and the primary study selected for the well was an aquifer study, then the well was included in the data set.

Every sample collected by the NAWQA Program was coded with a parameter called purpose of site visit. The intent of this code was to identify the nature and purpose of each individual sample collected. For example, a ground-water sample analyzed for temporal characterization of water quality from a well must be distinguished from the first environmental sample collected from a well. For the national assessment of VOCs, only samples coded as the primary environmental sample were selected for analysis, and these samples represented the first environmental sample collected from each well. These samples were selected because the intent of this assessment was to characterize a time snapshot of water quality in aquifers throughout the country and not to characterize temporal variations in water quality at individual wells. Only one primary environmental sample was analyzed from each well, and the term sample, as used in this report, indicates a sample from a single well that represents a distinct geographic site.

As previously mentioned, the VOCs included in the NAWQA Program were selected through a rigorous selection procedure (Bender and others, 1999). Some samples in the retrospective data were analyzed for only a small subset of these VOCs. To avoid a highly variable number of samples among individual VOCs, a minimum of 17 of the 55 VOCs included in this assessment was required in each sample analyzed in the retrospective data. A value of 17 was identified on the basis of a natural break in the distribution of the number of VOCs analyzed per well.

Because of the variability in the reporting levels for VOCs, and in particular for the retrospective data, each sample was required to have 75 percent or more of the reporting levels for all VOCs less than or equal to 0.2 µg/L. Samples with less than 75 percent of the reporting levels less than or equal to 0.2 µg/L were excluded. This procedure ensured that the majority of VOCs were measured using a reasonably high-resolution analytical capability. Consequently, few analyses in the data set had reporting levels greater than 0.2 µg/L.

Finally, a distancing criterion was applied to all wells to reduce potential effects of spatial dependence. Wells were selectively removed using an algorithm that maximized the number of wells retained while maintaining an inter-well distance of at least 1 kilometer (km). A weighting factor was used in the spatial distancing that allowed NAWQA-sampled wells to be selectively retained while wells from the retrospective data were removed. This was done because, in general, data from NAWQA-sampled wells included more VOCs and lower laboratory reporting levels compared to the retrospective data.

A total of 3,498 wells in 98 aquifer studies covering 47 States were retained in the final data set for analysis of VOCs in ground water. Figure 4 shows the location of all the wells sampled in aquifer studies, and figure 5 shows the location of the centroid of wells for each aquifer study.

The use of water from wells sampled for the aquifer studies was characterized and also is shown in table 5. Domestic wells comprise slightly more than 60 percent of all wells sampled in aquifer studies. However, proportionate to the total, more monitoring wells and other wells were sampled in the retrospective data set compared to the NAWQA data set (table 5). The percentages of public wells and other well types were nearly equal in the data set. Less than 10 percent of all wells were monitoring wells, and less than 2 percent of all wells did not have a known water use.

As previously mentioned, NAWQA sampling targeted existing wells in aquifers, and these wells generally were domestic wells. Domestic wells also were preferentially selected in the retrospective data compilation. In NAWQA aquifer studies, domestic wells were preferred over other types of wells because of (1) the random distribution of domestic wells in many areas; (2) the shallow nature of domestic wells relative to public wells, which allowed sampling of the upper part of most aquifers; (3) the low-flow characteristics of domestic wells allowing less drawdown stress to the aquifer and thus less vertical integration of water through the aquifer; and (4) the prohibitive cost of installing new wells. If domestic wells were not available, other well types were sampled in the NAWQA aquifer studies.
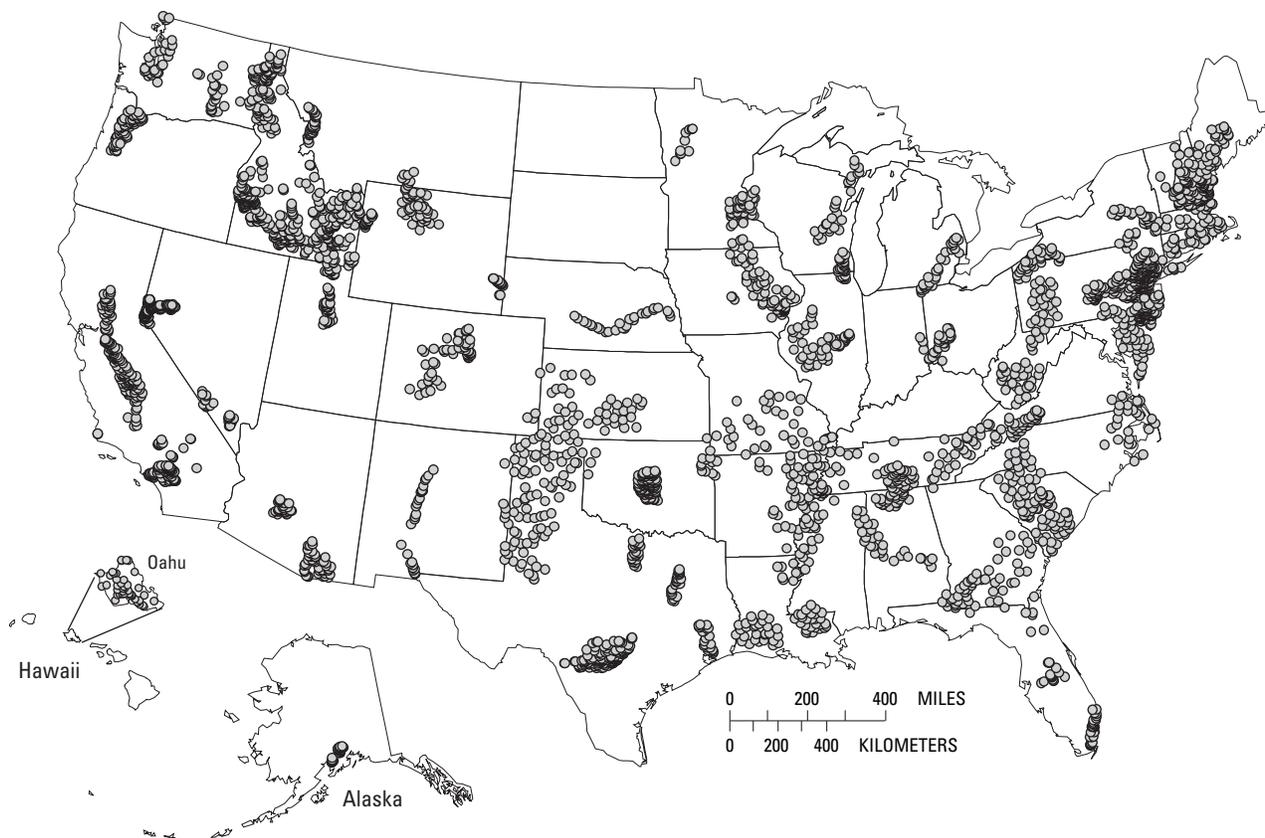
Base modified from U.S. Geological Survey digital data, 1:2,000,000, 1990
Albers Equal-Area Projection
North American Datum of 1983

Figure 4.   Locations of wells sampled in aquifer studies for a national assessment of volatile organic compounds.

Table 5.   Characterization of data for assessment of volatile organic compounds in ground water by water use and by source of data.

Use of water	NAWQA Aquifer Studies		Retrospective Aquifer Studies		Total number of wells	Total percent of wells
	Number of wells	Percent of total	Number of wells	Percent of total		
Domestic	1,621	70	517	43.6	2,138	61
Public supply	321	13.9	192	16.2	513	14.7
Monitoring	136	5.9	199	16.8	335	9.6
Other	224	9.7	237	20	461	13.2
Unknown	11	.5	40	3.4	51	1.5
Total	2,313	100	1,185	100	3,498	100
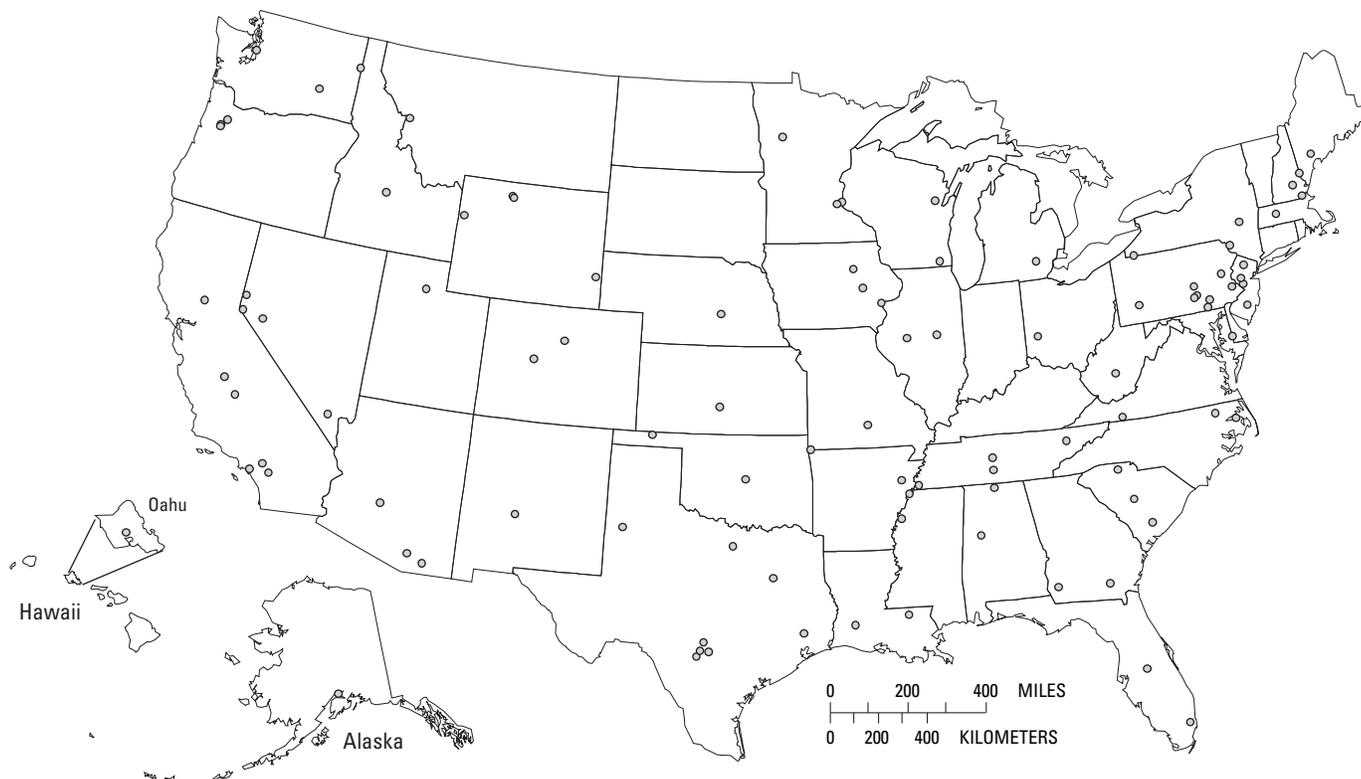
Base modified from U.S. Geological Survey digital data, 1:2,000,000, 1990
Albers Equal-Area Projection
North American Datum of 1983

Figure 5.   Locations of centroids of wells in aquifer studies included in a national assessment of volatile organic compounds.

VOC Data Used in Assessment of Drinking-Water Supply Wells

To determine the occurrence of VOCs in drinking-water supply wells, three sources of data were used (1) data from domestic wells and public wells sampled by the NAWQA Program in aquifer studies and in shallow ground-water studies throughout the United States during 1993–2002; (2) retrospective data from domestic wells and public wells compiled from Federal, State, and local agencies that sampled aquifers during 1985–1997; and (3) data from CWSs sampled as a collaborative effort of the USGS and other agencies during 1999–2000 as part of a national source-water survey. Details on the design of the NAWQA aquifer studies, the retrospective data, and the source-water survey were provided previously.

In addition to data from aquifer studies, data on VOCs in domestic and public wells were supplemented with NAWQA shallow ground-water studies. The number of domestic and public wells by data source is outlined in table 6. Although the shallow ground-water studies may introduce some bias with respect to input of VOCs from land-use activities, the number of domestic and public wells derived from these studies was small relative to the total. Only 11 percent of domestic wells and 1 percent of public wells were derived from NAWQA

shallow ground-water studies (table 6). The locations of domestic and public wells sampled for the national assessment of VOCs at an assessment level of 0.2 μg/L are shown in figures 6 and 7, respectively.

The NAWQA and retrospective data for drinking-water supply wells were selected using the same procedure as the data used in the assessment of VOCs in ground water. Selection criteria such as the intended purpose of the sample at the well, the analyte list and number of analytes per well, and laboratory reporting levels were considered. However, because of their small numbers, the domestic and public wells in the NAWQA shallow ground-water studies were not selected with respect to the distancing criterion.

The data on VOCs in public wells from the source-water survey did not undergo the same selection procedures as the NAWQA data because the design of this study already achieved an unbiased distribution of information. Because of the uniform design and collection of data in this survey, all samples from the source-water survey were analyzed for all 55 VOCs included in the national assessment (Ivahnenko and others, 2001). Also, wells sampled in the source-water survey had sufficient spatial distancing. Additional details on the design of the national source-water survey can be found in Ivahnenko and others (2001).
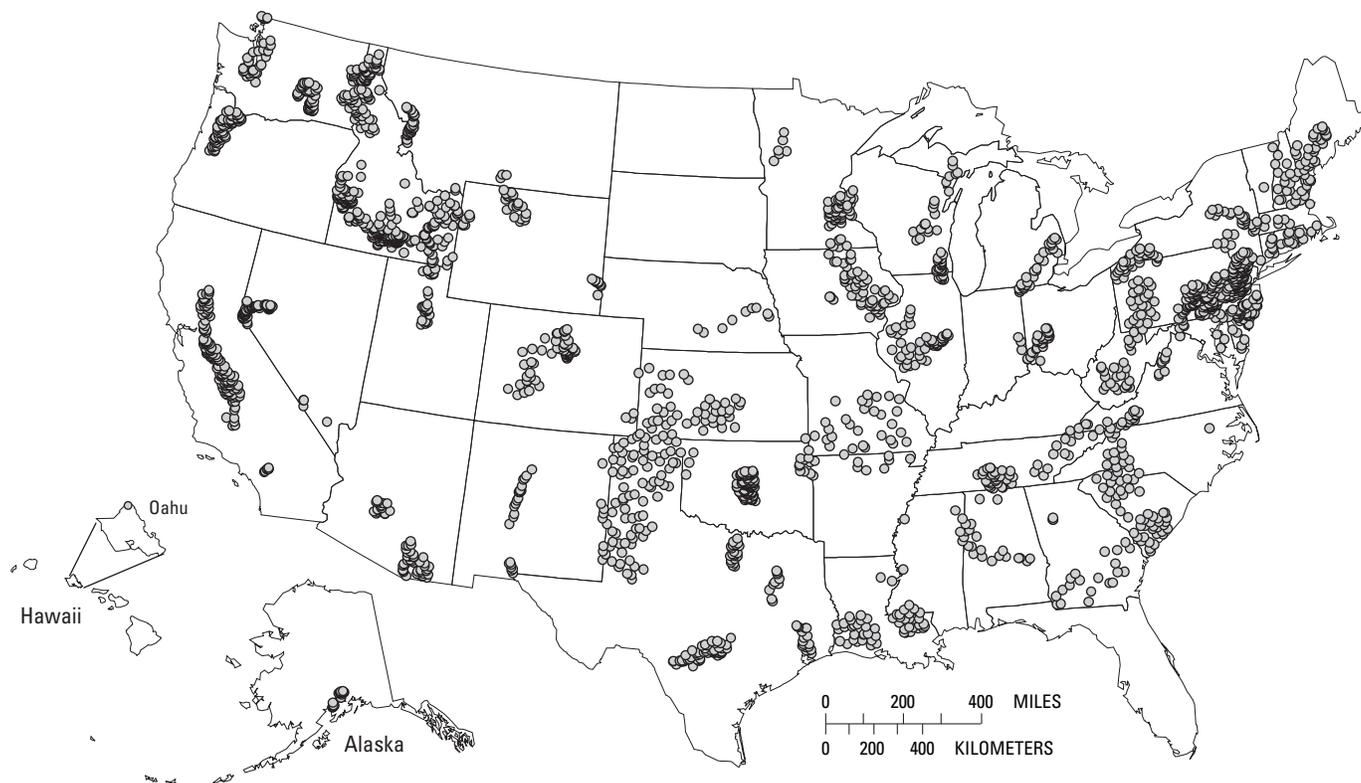
Base modified from U.S. Geological Survey digital data, 1:2,000,000, 1990
Albers Equal-Area Projection
North American Datum of 1983

Figure 6. Locations of domestic wells sampled for a national assessment of volatile organic compounds (VOCs) and included in the relational analyses of VOCs in domestic wells at an assessment level of 0.2 microgram per liter.

Table 6. Number of domestic and public wells used for assessment of VOCs by source of data.

Data source	Number of wells	Percent of wells
Domestic wells		
NAWQA aquifer studies	1,621	67.5
NAWQA shallow ground-water studies	263	11.0
Retrospective aquifer studies	517	21.5
Total	2,401	100
Public wells		
NAWQA aquifer studies	321	29.3
NAWQA shallow ground-water studies	8	.7
Retrospective aquifer studies	192	17.5
National source-water survey	575	52.5
Total	1,096	100

Analyses of the field QC data collected for the source-water survey indicated pervasive low-level contamination for many VOCs. It should be noted that all source-water environmental and field QC samples were collected by CWS personnel with instruction from the MWDSC (Grady, 2003). The sources of the low-level contamination in the QC samples could not be determined and contamination of source-water samples associated with the QC samples was presumed. The contamination prevented reporting the occurrence of VOCs at concentrations less than the MRL for each compound. In the source-water survey, the MRL for each compound was uniform at 0.2 µg/L (Grady, 2003). Because systematic contamination of some source water samples was identified in the source-water survey data set and about one-half of the public well data came from this survey, occurrence information for VOCs in public wells was reported only at the 0.2-µg/L assessment level.
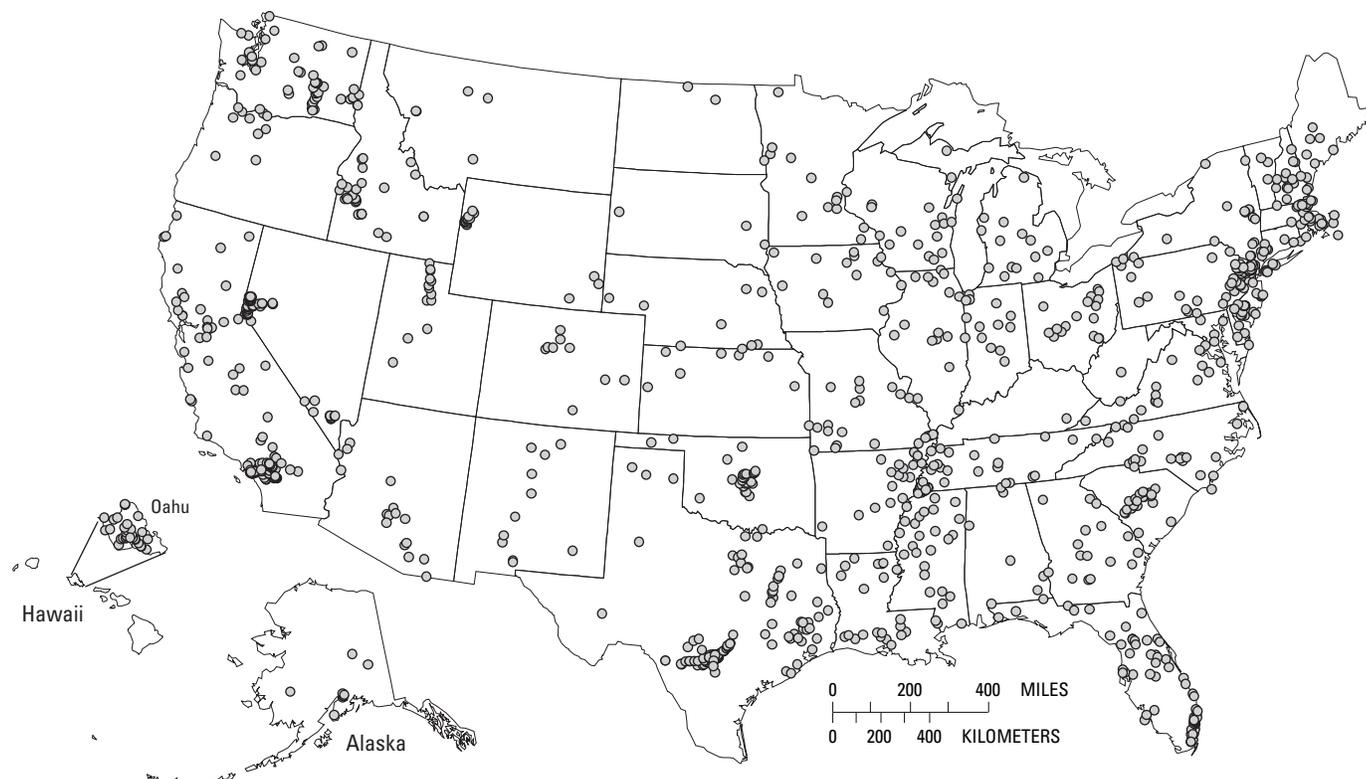
Base modified from U.S. Geological Survey digital data, 1:2,000,000, 1990
Albers Equal-Area Projection
North American Datum of 1983

Figure 7.   Locations of public wells sampled for a national assessment of volatile organic compounds (VOCs) and included in the relational analyses of VOCs in public wells at an assessment level of 0.2 microgram per liter.

VOC Data Used for Comparison to Drinking Water

In some cases, results from NAWQA sampling of domestic wells were compared to data on VOCs in drinking-water samples from a regional-scale survey of drinking water. Because water from domestic wells usually is not treated prior to use, results from domestic wells may reflect the quality of tap water used by many rural households.

Data on VOCs in drinking water from 12 New England and Mid-Atlantic States were compiled by the USGS and various other agencies (Grady and Casey, 1999). Hereafter, this survey is referred to as the drinking-water survey. The purpose of this survey was to describe the occurrence and distribution of VOCs in public drinking water supplied by CWSs in these 12 States. These States were selected for assessment because they generally are densely populated, have a long-term history of urbanization, and are areas of high use of public water supply (Grady and Casey, 1999). Details on the design and approach of the drinking-water survey can be found in Grady

and Casey (1999). Details on the results of the drinking-water survey can be found in Grady and Casey (2001).

The drinking-water survey data were samples of treated drinking water collected prior to distribution to meet the requirements of the Safe Drinking Water Act (SDWA). The samples were collected during 1993–1998 and were analyzed by various State and private laboratories. CWSs can be supplied exclusively by surface water, exclusively by ground water, or supplied by a combination of surface and ground water. Only data from CWSs supplied exclusively by ground water were used in a national assessment of VOCs.

A total of 1,695 CWSs with ground-water sources had data on VOCs in drinking water. Most analyses for SDWA compliance use USEPA methods 502.2 or 524.2. In most cases, drinking-water samples routinely are analyzed for 21 regulated and 21 unregulated VOCs (Grady and Casey, 2001). Data for 51 of the 55 VOCs included in the national assessment of VOCs were available in the drinking-water survey. However, for a national assessment of VOCs, only results for chlorinated solvents in domestic wells were compared to results from the drinking-water survey.

Reporting levels for VOCs in the drinking-water survey were variable. The median reporting level for most VOCs was 0.5 µg/L. Although this value is higher than the first-tier assessment level of 0.2 µg/L, the range in the reporting levels in the drinking-water survey extended below 0.2 µg/L. Additionally, the detection frequencies of many VOCs in drinking water were not different at assessment levels of 0.5 µg/L and 0.2 µg/L. Therefore, the first-tier assessment level of 0.2 µg/L was used for comparisons of VOCs detection frequencies between domestic wells and the drinking-water survey.

VOC Data Used in Relational Analyses

In a national assessment of VOCs, relational analyses were performed for three sets of data (1) data from aquifer studies, (2) data from domestic wells, and (3) data from public wells. For relational analyses of VOCs in aquifer studies, only data from the NAWQA aquifer studies and only data that were analyzed using the new low-level analytical method were used. As mentioned previously, these low-level data are a subset of data from the aquifer studies and included data collected by NAWQA Study Units that started in 1994 or 1997. The low-level data were used in the relational analyses without an assessment level application so that the resolving power of the data could be maximized.

Explanatory analyses were performed for 10 frequently detected VOCs in aquifer studies in samples from 1,687 wells. The 10 VOCs were chloroform, toluene, 1,2,4-trimethylbenzene, perchloroethene, 1,1,1-trichloroethane, chloromethane, MTBE, trichloroethene, methylene chloride, and bromodichloromethane, in order of decreasing detection frequency. Table 7 shows the distribution of the wells used in the explanatory analyses for aquifers by water use.

Table 7. Distribution of wells used in the explanatory analysis of volatile organic compounds in aquifers by water use.

Water use	Number of wells	Percent of wells
Domestic	1,205	71.4
Public supply	241	14.3
Monitoring	70	4.1
Other	171	10.2
Total	1,687	100
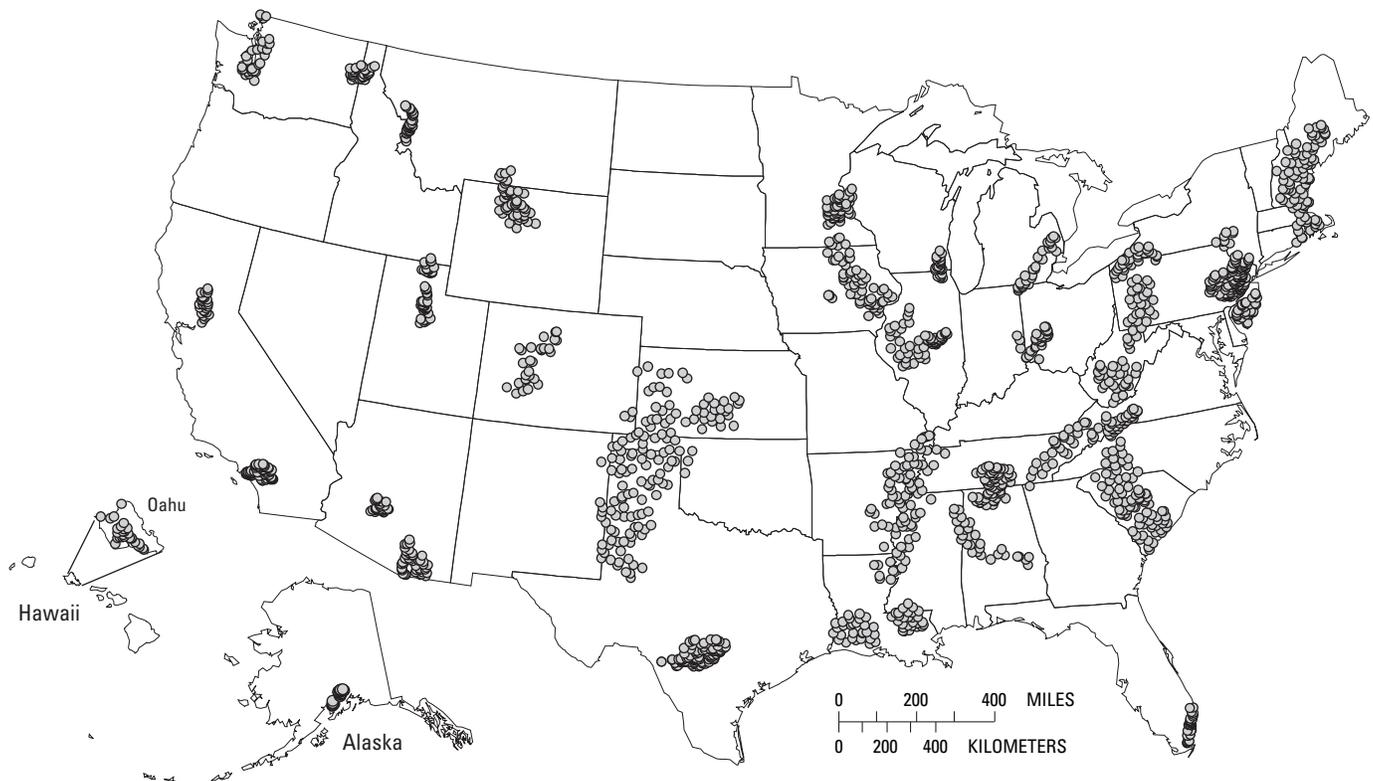
Base modified from U.S. Geological Survey digital data, 1:2,000,000, 1990
Albers Equal-Area Projection
North American Datum of 1983

Figure 8. Locations of wells used in the relational analyses of volatile organic compounds in aquifers.

Because the data used for the relational analyses of VOCs in aquifers were a subset of the NAWQA aquifer study data, they underwent the same selection procedures as the full data set used in the assessment of VOCs in aquifers. Figure 8 shows the geographic distribution of wells used in the relational analyses of VOCs in aquifers.

For relational analyses of VOCs in domestic wells, data from the NAWQA Program and retrospective data were used. The NAWQA data were from both aquifer and shallow ground-water studies. Because of the variability in reporting levels in this data set, the relational analyses for domestic wells were performed at both assessment levels tiers. Analyses were performed for 6 frequently detected VOCs at the 0.2-μg/L assessment level and for 10 frequently detected VOCs at the 0.02-μg/L assessment level. At an assessment level of 0.2 μg/L, the VOCs analyzed were chloroform, MTBE, perchloroethene, 1,1,1-trichloroethane, dichlorodifluoromethane, and toluene, in order of decreasing detection frequency. At an assessment level of 0.02 μg/L, the VOCs analyzed were chloroform, toluene, 1,2,4-trimethylbenzene, chloromethane, perchloroethene, MTBE, methylene chloride, 1,1,1-trichloroethane, dichlorodifluoromethane, and trichloroethene, in order of decreasing detection frequency.

Data from 2,401 domestic wells were available for relational analyses at an assessment level of 0.2 μg/L, and data from 1,208 domestic wells were available for relational analyses at an assessment level of 0.02 μg/L. Domestic wells in aquifer studies underwent the data selection procedures outlined previously. However, domestic wells in shallow ground-water studies did not undergo any of the data selection procedures. Only about 11 percent of domestic wells were from NAWQA shallow ground-water studies at an assessment level of 0.2 μg/L. Figure 6 shows the locations of domestic wells with data for relational analyses at an assessment level of 0.2 μg/L. The locations of domestic wells with data for relational analyses at an assessment level 0.02 μg/L are shown in figure 9.

For relational analyses of VOCs in public wells, data from the NAWQA Program and from the source-water survey were used. Like domestic wells, the NAWQA data for public wells were from aquifer studies and shallow ground-water studies. Only data from public wells in aquifer studies underwent the selection procedures outlined previously. Data from public wells in the NAWQA shallow ground-water studies and the source-water survey did not undergo any selection procedures. Less than 1 percent of public wells were from NAWQA
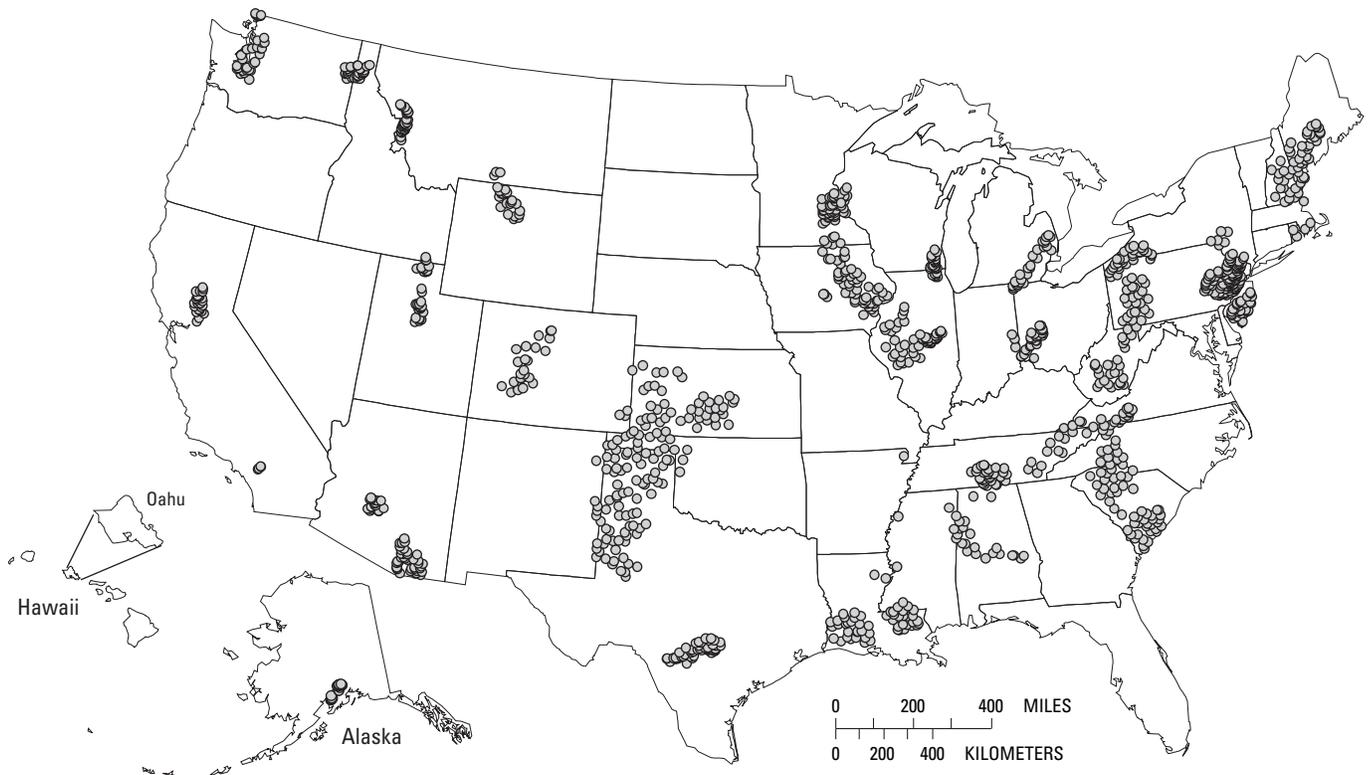

Base modified from U.S. Geological Survey digital data, 1:2,000,000, 1990
Albers Equal-Area Projection
North American Datum of 1983

Figure 9. Locations of domestic wells used in the relational analyses of volatile organic compounds at an assessment level of 0.02 microgram per liter.

shallow ground-water studies. Because VOC concentrations in public well samples from the source-water survey were not reported at less than 0.2 µg/L, this assessment level was used for the relational analyses. Analyses were performed for 9 frequently detected VOCs and for a total of 1,096 wells. The VOCs were chloroform, MTBE, perchloroethene, bromoform, dibromochloromethane, trichloroethene, bromodichloromethane, 1,1,1-trichloroethane, and 1,1-dichloroethane, in order of decreasing detection frequency. Figure 7 shows the locations of public wells with data for relational analyses at 0.2 µg/L.

Ancillary Data Used in Relational Analyses

A variety of ancillary data were used in the relational analyses. Table 8 lists the ancillary variables used in the relational analyses, the units for each variable, a description of the variable, coding of the variable in the analysis, and the source of the data. In the relational analyses, density, percent, polygon, and point data were averaged for a 500m radius around each well. In some cases, density data also were estimated for a 1-km radius around each well or as a point value for each well using linear interpolation.

Table 8.   Hydrogeologic and anthropogenic variables that were used in the logistic regression analyses.

[mm/yr, millimeter per year; in/hr, inch per hour; g/cm^3, gram per cubic centimeter; °C, degrees Celsius; mg/L, milligram per liter; µS/cm, microsiemens per centimeter; km^2, kilometer squared; USGS, U.S. Geological Survey; GWSI, USGS Ground-Water Site Inventory; QWDATA, USGS Water-Quality database; NAWQA, USGS National Water-Quality Assessment Program; USEPA, U.S. Environmental Protection Agency; CIESIN, Consortium for International Earth Science Information Network; TRI, Toxics Release Inventory; CERCLA, Comprehensive Environmental Response, Compensation, and Liability Act; RCRA, Resource Conservation and Recovery Act; MTBE, methyl *tert*-butyl ether]

Variable	Units	Description	Coding	Source
		Hydrogeologic variables		
Recharge	mm/yr	estimated mean annual recharge	continuous	Wolock (2003)
Soil permeability	in/hr	average soil permeability by soil unit	continuous	Wolock (1997)
Soil sand	percent	average soil sand content by soil unit	0 – 100	Wolock (1997)
Soil silt	percent	average soil silt content by soil unit	0 – 100	Wolock (1997)
Soil clay	percent	average soil clay content by soil unit	0 - 100	Wolock (1997)
Soil organic matter	percent	average organic matter content by soil unit	0 - 100	Wolock (1997)
Soil bulk density	g/cm^3	average bulk density of soil by soil unit	continuous	Wolock (1997)
Soil erodibility	unitless	soil erosion rate per soil erosion unit	0.02 – 0.69	Wolock (1997)
Vertical soil permeability	in/hr	average vertical soil permeability by soil unit	continuous	Wolock (1997)
Hydric soils	percent	average percent hydric soils by soil unit	0 - 100	Wolock (1997)
Available water capacity	fraction	average water fraction by soil unit	0 - 1	Wolock (1997)
Slope of land surface	percent	average slope of land surface by soil unit	0 - 100	Wolock (1997)
Seasonal water level	feet	average depth to seasonally high water table by soil unit	continuous	Wolock (1997)

Table 8. Hydrogeologic and anthropogenic variables that were used in the logistic regression analyses.—Continued

Variable	Units	Description	Coding	Source
Hydrogeologic variables—Continued				
Soil thickness	inches	average depth to bedrock by soil unit	continuous	Wolock (1997)
Precipitation	centimeters	estimated mean annual precipitation	continuous	U.S. Dept. of Commerce (1995)
Air temperature	°C	estimated mean annual air temperature	continuous	U.S. Dept. of Commerce (1995)
Well casing diameter	feet	average casing diameter	continuous	GWSI
Well depth	feet	total depth of well	continuous	GWSI
Water level	feet	average water level in well		GWSI
Depth to top of screened interval	feet	depth to the top of the screened interval in the well	continuous	GWSI
Aquifer confinement	unitless	confining condition of the aquifer	1 – unconfined; 0.5 – mixed; 0 - confined	GWSI
Temperature of ground water	°C	average temperature of water in the well	continuous	GWSI
Dissolved oxygen	mg/L	average dissolved oxygen content of water in the well	continuous	QWDATA
Specific conductance	µS/cm	average specific conductance of water in the well	continuous	QWDATA
Anthropogenic variables				
Population	persons/km^2	block group population	continuous	Bureau of the Census (1991); CIESIN (1995); Dobson and others (2000)
Septic sewerage	percent	block group percent of households using septic sewerage	0 - 100	Bureau of the Census (1991)
Population using septic sewerage	persons/km^2	block group population times percent using septic sewerage	continuous	Bureau of the Census (1991)
Public sewerage	percent	block group percent of households using public sewerage	0 - 100	Bureau of the Census (1991)
Other sewerage	percent	block group percent of households using other sewerage	0 - 100	Bureau of the Census (1991)
Public-water-supply usage	percent	block group percent of households using public water supply	0 - 100	Bureau of the Census (1991)
Domestic-water-supply usage	percent	block group percent of households using domestic water supply	0 - 100	Bureau of the Census (1991)
Households with drilled wells	percent	block group percent of households having drilled wells	0 - 100	Bureau of the Census (1991)
Households with dug wells	percent	block group percent of households having dug wells	0 - 100	Bureau of the Census (1991)
Households with other water service	percent	block group percent of households having other water service	0 - 100	Bureau of the Census (1991)

Table 8. Hydrogeologic and anthropogenic variables that were used in the logistic regression analyses.—Continued

Variable	Units	Description	Coding	Source
Anthropogenic variables—Continued				
Year of home construction	years	block group median age	0 - 100	Bureau of the Census (1991)
Leaking gasoline underground storage tanks	count	number of sites within 1 km of well	continuous	Vista Information Solutions (1999)
Leaking underground storage tanks associated with dry cleaners	count	number of sites within 1 km of well	continuous	Vista Information Solutions (1999)
Gasoline underground storage tanks	count	number of sites within 1 km of well	continuous	Vista Information Solutions (1999)
Dry-cleaning underground storage tanks	count	number of sites within 1 km of well	continuous	Vista Information Solutions (1999)
MTBE use in gasoline	binary	use of MTBE in gasoline	1 – high use 0 – low or no use	USEPA (2003c)/TRW Petroleum Technologies, written commun., 1999
Urban land use	percent	average urban land use around well	0 - 100	USGS (1990); Wright and others (1995); Vogelmann and others (2001); C.V. Price, USGS, written commun., 2004
Agricultural land use	percent	average agricultural land use around well	0 - 100	USGS (1990); Wright and others (1995); Vogelmann and others (2001); C.V. Price, USGS, written commun., 2004
Undeveloped land use	percent	average undeveloped land use around well	0 - 100	USGS (1990); Wright and others (1995); Vogelmann and others (2001); C.V. Price, USGS, written commun., (2004)
Roads	percent	average percent road area around well	0 - 100	Bureau of the Census (1991)
TRI sites	count	number of sites within 1 km of well	continuous	USEPA (2004c)
CERCLA sites	count	number of sites within 1 km of well	continuous	USEPA (2004c)
RCRA hazardous waste facilities	count	number of facilities within 1 km of well	continuous	USEPA (2004c)
Use of water from the well	categorical	major use of water from the well	1 – public supply 0 – domestic supply	GWSI

Hydrogeologic Variables

The hydrogeologic variables used in the relational analyses included 24 variables listed in table 8. Recharge represented the potential transport of VOCs from the ground surface or shallow subsurface to the water table or potentiometric surface. It was expected that increased recharge would increase the probability of detecting a VOC because there would be less time for transformations or other losses to occur. Mean annual recharge was computed by multiplying a grid of base-flow index (BFI) values (Wolock, 2003) by a grid of derived mean-annual runoff values (Gebert and others, 1987). The BFI was calculated at each stream gage using the Wahl and Wahl (1995) hydrograph separation technique. Recharge was available as a 1-km grid of average annual recharge in millimeters per year. Values of recharge for each well were obtained by linear interpolation between grid-cell nodes.

This estimation of recharge relies upon two assumptions: (1) long-term ground-water storage does not change (that is, ground-water recharge is equal to ground-water discharge); and (2) the BFI reasonably represents, over the long term, the percentage of ground-water discharge in streamflow. Stream gages on large river systems in the United States were not included in the runoff values, and thus estimates of recharge were representative of local, and possibly intermediate, ground-water-flow systems. Recharge to the deep regional ground-water-flow systems probably was not reflected in the recharge estimate. In addition to natural recharge, irrigation may augment the transport of VOCs to ground water in some areas. However, because of evapotranspiration, the increased transport potential of irrigation probably was not reflected in the recharge estimates. In some areas with high irrigation and high evapotranspiration, the recharge estimates may substantially underestimate the true recharge to ground water and thus the true transport potential of VOCs to ground water.

Thirteen different variables were used to estimate various soil parameters that might either facilitate or impede the transport of VOCs from sources located at or near the ground surface to the water table or potentiometric surface (table 8). For example, it was expected that increased soil permeability would increase the probability of detecting a VOC because of the lower resistance to flow offered by more permeable soils. It also was expected that increased soil sand content would increase the probability of detecting a VOC because of the increased interconnected porosity associated with increased sand content of the soil. It also was expected that increased soil percent organic matter would decrease the probability of detecting a VOC because of increased adsorption of VOCs associated with increasing organic matter in soil.

All soil information was obtained from the National Resource Conservation Service State Soil Geographic (STATSGO) data set (Wolock, 1997). The soil characteristics were weighted average values, by soil unit, from the STATSGO database and had varying units (table 8). These values were placed into a 1-km resolution grid for the conterminous United States. Because of their spatially generalized nature, the STATSGO data cannot accurately estimate average soil characteristics for small areas. However, when averaged over large areas, the soil characteristics from STATSGO are useful as explanatory variables in regional and national water-quality assessment studies. Values of soil characteristics for each well were obtained by linear interpolation between grid-cell nodes. In most cases, the soil parameter characteristics were numerically continuous, whereas others were fractions (table 8).

Estimated mean annual precipitation and air temperature represented controls on the transport of VOCs. Precipitation represented the driving force behind the transport of VOCs from the ground surface or shallow subsurface to the water table or potentiometric surface. It was expected that increased precipitation would increase the probability of detecting a VOC because of increased recharge. Air temperature was believed to be related to the biologic activity necessary to transform VOCs. It was expected that increased air temperature would decrease the probability of detecting a VOC because of increased biologic activity and thus increased biotransformation of VOCs in the vadose zone.

Data on precipitation and air temperature were obtained from the National Climate Data Center (NCDC) and were estimated annual averages from 1961–1990 data (U.S. Department of Commerce, 1999). The data used to compute the annual means were obtained from more than 8,000 sites around the country. Precipitation was expressed as centimeters per year and air temperature as annual average in degrees Celsius. Climatological data were placed into a point coverage of mean annual precipitation and mean annual air temperature at measuring sites. Values of precipitation and air temperature for each ground-water sampling point were obtained by linear interpolation between data points.

Well-specific information such as casing diameter, well depth, water level, depth to the top of the screened interval, aquifer confinement, ground-water temperature, dissolved-oxygen content, and specific conductance all represented various hydrogeologic conditions of the aquifer that could affect the transport, movement and fate of VOCs. For example, it was expected that increasing depth of the well would decrease the probability of detecting a VOC because of the increased time needed to transport VOCs from the surface to the water table or potentiometric surface and thus the increased chance for transformations or other losses to occur. It also was expected that confined aquifers would have a decreased probability of detecting a VOC relative to unconfined aquifers because of the increased time needed for recharge to move through confining layers, increasing the chance for losses of VOCs, like transformations or adsorption, to occur.

Well and water-level information were available from the USGS Water-Quality database (QWDATA) and Ground-Water Site Inventory (GWSI) database. In most cases, average values of variables were computed for each well from available data. Values of ground-water temperature, specific conductance, and dissolved oxygen were obtained from samples collected at, or as close as possible to, the time of sampling for VOCs. Values

were expressed in various units, but all were continuous with the exception of aquifer confinement, which was expressed as a category. The value 1 was assigned to unconfined aquifers, 0.5 was assigned to aquifers that were mixed, and 0 was assigned to confined aquifers.

Anthropogenic Variables

The 24 anthropogenic variables that were used in the relational analyses are listed in table 8. The purpose of these variables was to represent a variety of human activities that contribute to the source of VOCs in ground water or facilitate the transport and fate of VOCs in ground water. Anthropogenic variables that were considered to represent sources of VOCs to the environment included population, septic sewerage, population using septic sewerage, public sewerage, other sewerage, year of home construction, leaking gasoline underground storage tanks, leaking underground storage tanks associated with dry cleaners, gasoline underground storage tanks, underground storage tanks associated with dry cleaners, MTBE usage in gasoline, land use, road density, and USEPA regulated sites including sites listed for regulation under the Resource Conservation and Recovery Act (RCRA), the TRI, and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). Because these variables represent potential sources of VOCs to the environment, an increase in any of these variables was expected to increase the probability of detecting a VOC.

Data on population, septic sewerage, population using septic sewerage, public sewerage, other sewerage, year of home construction, and roads were available from the 1990 census (Bureau of the Census, 1991). Population data were available in three forms: (1) census block group data (Bureau of Census, 1991); (2) grids from the Consortium for International Earth Science Information Network (1995); and (3) grids from the LandScan data set (Dobson and others, 2000). The remainder of census data was derived from block group census information from the 1990 census (Bureau of the Census, 1991).

Information on the locations of underground storage tanks came from the StarView database published by Vista Information Solutions (1999). Land-use information was obtained from National Land Cover Dataset (NLCD) (Vogelmann and others, 2001) and from the USGS Geographic Information and Retrieval System (U.S. Geological Survey, 1990; Wright and others, 1995). Land-use data from NLCD was enhanced by the USGS (C.V. Price, U.S. Geological Survey, written commun., 2004). Locations of USEPA regulated sites were obtained from the Envirofacts database (U.S. Environmental Protection Agency, 2004c). Information on the use of MTBE in gasoline as an oxygenate was available from the USEPA (U.S. Environmental Protection Agency, 2003c) and TRW Petroleum Technologies (TRW, written commun., 1999).

Other anthropogenic variables included public-water-supply usage, domestic-water-supply usage, households with drilled wells, households with dug wells, households with

other water service, and use of water from the well. These variables represented surrogates for transport and fate controls on the occurrence of VOCs such as land use, areas contributing recharge to the well, pumping stress to the aquifer, and flowpath length. These variables are less precise because they may represent several different processes or controls. For example, an increase in public-water-supply density was expected to increase the probability of detecting a VOC because of a concomitant increase in population density, urban land use, and aquifer stress in these areas. Conversely, an increase in domestic-water-supply density was expected to correspond to a decrease in public-water-supply density and a decrease the probability of detecting a VOC because of lower population density, urban land use, and aquifer stress in these areas. Public wells were expected to have a greater probability of detecting a VOC compared to domestic wells because public wells generally have higher pumping rates and larger areas contributing recharge and thus have the ability to capture more potential sources of VOCs. All of these variables, with the exception of use of water from the well, were derived from block group census information from the 1990 census (Bureau of the Census, 1991). Data on use of water from the well was available from the USGS GWSI database.

Other Ancillary Data

Transformations are an important natural control on the fate of VOCs in ground water. Once released to the environment, VOCs are continually acted on by physical and chemical (abiotic) or biological (biotic) activities that can transform them. Important abiotic transformation processes include hydrolysis, photolysis, reduction, hydrogenolysis, dehydrogenation, and oxidation. Although most VOCs have sufficient free energy to undergo abiotic reactions, the potential is rarely met except under very reducing conditions and not without mediation by bacteria (Pankow and Cherry, 1996). Thus, most transformations in the environment, and especially in ground water, probably are biotic. Biotic processes for transformation of VOCs can be either aerobic or anaerobic and occur through three possible pathways: (1) as an electron acceptor, (2) as an electron donor, and (3) co-metabolism.

Biotransformation rate constants were estimated for many of the 55 VOCs and for all possible pathways. The rate constant estimates were based on documented laboratory studies using aquifer materials (grab samples of sediment and/or ground water) and *in situ* studies of ground-water materials. Biotransformation rate constants were obtained from publications spanning from 1980 to 2003. Additionally, rate constants were compiled from USEPA summary reports (U.S. Environmental Protection Agency, 1999a, 1999b). These summaries were based on studies of aerobic and anaerobic biodegradation. Half-lives of VOCs in ground water, based on both experimental data and estimation techniques, were reviewed and compiled by Howard and others (1991).

Production of VOCs, when coupled with biodegradation, may aid in the understanding of VOC occurrence in ground water. Production values for VOCs were compiled for 1960 through 2000. Production in the United States, in addition to imports and exports, was obtained from the Chemical Products Synopsis, a reporting service of the Mannsville Chemical Products Corporation (1983–2002). Additional production data for gasoline hydrocarbons were obtained from the U.S. Department of Energy Information Administration (2003). Estimations of the volume of various gasoline hydrocarbons in gasoline were based on Canadian data (Canadian Petroleum Products Institute, 1994).

Production of VOCs frequently is used as an indicator of the releases of compounds to the environment. However, estimating VOC releases to the environment using production as a surrogate must be done with caution. Production volume may not correlate well with release volume to the environment. Also, VOCs produced and/or purchased within a specific timeframe are not necessarily used during that period. Finally, VOCs produced in one geographic area, or country, may be used elsewhere. Although Federal, State, and local government have created toxic release databases, VOC releases into the environment remain difficult to assess.

Finally, the estimated age of ground water represented another important hydrogeologic control on the fate of VOCs in ground water. The more time available for abiotic and biotic transformation processes to occur, the less likely it is that VOCs will be detected in ground water. Age date information for ground-water samples was estimated from direct analytical methods including chlorofluorocarbons and tritium, and from indirect methods such as ground-water-flow modeling. Age date information was only available for a relatively small subset of NAWQA-sampled wells.

Summary

The Volatile Organic Compound (VOC) Synthesis team of the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program developed an approach for a national assessment of VOCs in the Nation's ground water and drinking-water supply wells, specifically domestic and public wells. The purpose of the assessment of VOCs was to provide a national overview of ground-water quality. This report describes the development of the approach, documents the design of the analyses and planning efforts, and provides supporting technical information.

Data on VOCs in samples from aquifers and from domestic and public wells had three sources: (1) NAWQA sampling of ground water in aquifer studies and of shallow ground water in areas of agricultural or urban land use from 1993-2002; (2) retrospective data from other Federal, State, and local agencies that sampled ground water in aquifer studies from 1985-1997; and (3) sampling of ground water used as a source for community water systems from 1999-2000 (source-water survey). The geographic scope of sampling for all three data sources was nationwide. For some analyses, data from a survey of drinking water of community water systems in 12 New England and Mid-Atlantic States also were used.

Data for assessing VOCs in ground water came from the NAWQA sampling of aquifers and from retrospective data. Domestic wells were the most commonly sampled type of well in these aquifers studies. Data for assessing VOCs in domestic well samples came from the NAWQA sampling of aquifers and shallow ground water and from retrospective data. Data for assessing VOCs in public well samples came from NAWQA sampling of aquifers and shallow ground water and from the source-water survey.

Fifty-five VOCs were included in a national assessment of VOCs. All ground-water samples for VOC analysis were collected using consistent, prescribed field protocols and were analyzed using approved analytical methods. All ground-water collection activities included quality-control methods, including the collection of various quality control samples, to ensure the quality of the data. Likewise, laboratory procedures included approved methods and quality-control samples to further ensure data quality.

Comparisons of detection frequencies and concentrations among individual VOCs, groups of VOCs, networks, and data sets were performed using two assessment levels: (1) an assessment level of 0.2 microgram per liter (μg/L) and (2) an assessment level of 0.02 μg/L. Selection of the 0.2-μg/L assessment level was based on historical reporting levels used by the USGS National Water Quality Laboratory (NWQL) prior to April 1996, and selection of the 0.02-μg/L assessment level was based on a new, low-level analytical method developed by the NWQL and used since April 1996. To communicate the potential health significance of water-quality findings, VOC concentrations in samples from domestic and public wells were compared to U.S. Environmental Protection Agency Maximum Contaminant Levels and Health-Based Screening Levels.

Relational analyses, using multivariate logistic regression, were performed on VOC data from aquifers, domestic wells, and public wells to better understand the natural and anthropogenic factors related to the occurrence of VOCs. For the relational analyses of data from aquifers, only NAWQA data analyzed using the new low-level analytical method were used. This was a subset of data from aquifers and included only data from NAWQA Study Units that started work in 1994 or 1997. For the relational analyses of data from aquifers, 10 frequently detected VOCs were analyzed using no assessment level. For the relational analyses of data from domestic wells, six frequently detected VOCs were analyzed at an assessment level of 0.2 μg/L, and 10 frequently detected VOCs were analyzed at an assessment level of 0.02 μg/L. For the relational analyses of data from public wells, nine frequently detected VOCs were examined at an assessment level of 0.2 μg/L.

A variety of ancillary data were used in the relational analyses that represented a range of hydrogeologic and anthropogenic factors that control the source, transport, and

fate of VOCs in ground water. Anthropogenic variables mostly represented the sources of VOCs to ground water, whereas hydrogeologic variables mostly represented the transport and fate of VOCs in ground water.

References

Ashford, N.A., and Miller, C.S., 1991, Chemical exposures—Low levels and high stakes: New York, Van Nostrand Reinhold, 214 p.

Bender, D.A., Zogorski, J.S., Halde, M.J., and Rowe, B.L., 1999, Selection procedure and salient information for volatile organic compounds emphasized in the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 99–182, 32 p.

Bloemen, H.J.Th., and Burn, J., 1993, Chemistry and analysis of volatile organic compounds in the environment: New York, Blackie Academic and Professional, 290 p.

Bureau of the Census, 1991, Census of population and housing, 1990—Public Law 94–171 data (United States) (machine readable data files): Washington, D.C., The Bureau (producer and distributor).

Canadian Petroleum Products Institute, 1994, Composition of Canadian summer and winter gasolines—1993: Alberta, Canada, Canadian Petroleum Products Institute Report 94–5.

Clawges, R.M., Rowe, B.L., and Zogorski, J.S., 2001, National survey of MTBE and other VOCs in community drinking-water sources: U.S. Geological Survey Fact Sheet FS–064–01, 4 p.

Connor, B.F., Rose, D.L., Noriega, M.C., Murtagh, L.K., and Abney, S.R., 1998, Methods of analysis by the U.S. Geological Survey National Water-Quality Laboratory—Determination of 86 volatile organic compounds in water by gas chromatography/mass spectrometry, including detections less than reporting limits: U.S. Geological Survey Open-File Report 97–829, 78 p.

Consortium for International Earth Science Information Network (CIESIN), 1995, Socioeconomic Data and Applications Center (SEDAC), Archive of Census Related Products: CIESIN/SEDAC, accessed July 21, 1998, at *http://sedac. ciesin.org/plue/cenguide.html*

Delzer, G.C., and Ivahnenko, Tamara, 2003, Occurrence and temporal variability of methyl *tert*-butyl ether and other volatile organic compounds in select sources of drinking water—Results of the focused survey: U.S. Geological Survey Water-Resources Investigations Report 02–4084, 65 p.

Dobson, J.E., Bright, E.A., Coleman, P.R., Durfee, R.C., and Worley, B.A., 2000, A global population database for estimating population at risk: Photogrammetric Engineering & Remote Sensing, v. 66, no. 7, p. 849–857.

Fishman, M.J., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93–125, 217 p.

Gebert, W.A., Graczyk, D.J., and Krug, W.R., 1987, Average annual runoff in the United States, 1951–80: U.S. Geological Survey Hydrologic Investigations Atlas HA–710, scale 1:7,500,000, 1 sheet.

Gilliom, R.J., Alley, W.M., and Gurtz, M.E., 1995, Design of the National Water-Quality Assessment Program—Occurrence and distribution of water-quality conditions: U.S. Geological Survey Circular 1112, 33 p.

Grady, S.J., 2003, A national survey of methyl *tert*-butyl ether and other volatile organic compounds in drinking water sources—Results of the random survey: U.S. Geological Survey Water-Resources Investigations Report 02–4079, 85 p.

Grady, S.J., and Casey, G.D., 1999, A plan for assessing the occurrence and distribution of methyl *tert*-butyl ether and other volatile organic compounds in drinking water and ambient ground water in the Northeast and Mid-Atlantic regions of the United States: U.S. Geological Survey Open-File Report 99–207, 36 p.

Grady, S.J., and Casey, G.D., 2001, Occurrence and distribution of methyl *tert*-butyl ether and other volatile organic compounds in drinking water in the Northeast and Mid-Atlantic regions of the United States, 1993–98: U.S. Geological Survey Water-Resources Investigations Report 00–4228, 123 p.

Helsel, D.R., and Hirsch, R.M., 1993, Statistical methods in water resources: Amsterdam, The Netherlands, Elsevier Science, 522 p.

Howard, P.H., Boethling, R.S., Jarvis, W.F., Meylan, W.M., and Michalenko, E.M., 1991, Environmental degradation rates: Chelsea, Mich., Lewis Publishers, 725 p.

Ivahnenko, Tamara, and Barbash, J.E., 2004, Chloroform in the hydrologic system—Sources, transport, fate, occurrence, and effects on human health and aquatic organisms: U.S. Geological Survey Scientific Investigations Report 2004–5137, 34 p.

Ivahnenko, Tamara, Grady, S.J., and Delzer, G.C., 2001, Design of a national survey of methyl *tert*-butyl ether and other volatile organic compounds in drinking-water sources: U.S. Geological Survey Open-File Report 01–271, 42 p.

Koch, Bart; Dale, Melissa; Zogorski, John; Delzer, Gregory; Grady, Stephen; Ivahnenko, Tamara; Clawges, Rick; and Tratnyek, Paul, 2003, Occurrence of MTBE and VOCs in drinking-water sources of the United States: Denver, American Water Works Association Research Foundation Report #90954F, 189 p. and CD-ROM.

Koterba, M.T., Wilde, F.D., and Lapham, W.W., 1995, Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program—Collection and documentation of water-quality samples and related data: U.S. Geological Survey Open-File Report 95–399, 113 p.

Lapham, W.W., Moran, M.J., and Zogorski, J.S., 2000, Enhancements of non-point source monitoring of volatile organic compounds in ground water: Journal of the American Water Works Association, v. 36, no. 6, p. 1321–1334.

Lapham, W.W., Neitzert, K.M., Moran, M.J., and Zogorski, J.S., 1997, USGS compiles data set for national assessment of VOCs in ground water: Ground Water Monitoring and Remediation, v. 17, no. 4, p. 147–157.

Lapham, W.W., and Tadayon, Saeid, 1996, Plan for assessment of the occurrence, status, and distribution of volatile organic compounds in aquifers of the United States: U.S. Geological Survey Open-File Report 96–199, 44 p.

Lapham, W.W., Wilde, F.D., and Koterba, M.T., 1995, Ground-water data-collection protocols and procedures for the national water-quality assessment program—Selection, installation, and documentation of wells, and collection of related data: U.S. Geological Survey Open-File Report 95–398, 69 p.

Lapham, W.W., Wilde, F.D., and Koterba, M.T., 1997, Guidelines and standard procedures for studies of ground-water quality—Selection and installation of wells and supporting documentation: U.S. Geological Survey Water-Resources Investigations Report 96–4233, 110 p.

Mannsville Chemical Products Corporation, 1983–2002, Chemical products synopsis: Adams, New York, Mannsville Chemical Products [variously paged].

Menard, Scott, 2002, Applied logistic regression analysis: Thousand Oaks, Calif., Sage Publications, Inc., 111 p.

Moran, M.J., Clawges, R.M., and Zogorski, J.S., 2002, Methyl *tert*-butyl ether in ground and surface water of the United States, *in* Diaz, A.F., and Drogos, D.L., eds., Oxygenates in gasoline: Washington, D.C., American Chemical Society, p. 2–16.

Oblinger Childress, C.J., Foreman, W.T., Connor, B.F., and Maloney, T.J., 1999, New reporting procedures based on long-term method detection levels and some considerations for interpretations of water-quality data provided by the U.S. Geological Survey National Water Quality Laboratory: U.S. Geological Survey Open-File Report 99–193, 19 p.

Pankow, J.F., and Cherry, J.A., 1996, Dense chlorinated solvents: Portland, Oreg., Waterloo Press, 522 p.

Rose, D.L., and Schroeder, M.P., 1995, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of volatile organic compounds in water by purge and trap capillary gas chromatography/mass spectrometry: U.S. Geological Survey Open-File Report 94–708, 26 p.

Scott, Jon, 1990, Computerized stratified random site-selection approaches for design of a ground-water-quality sampling network: U.S. Geological Survey Water-Resources Investigations Report 90–4101, 109 p.

Squillace, P.J., Moran, M.J., Lapham, W.W., Price, C.V., Clawges, R.M., and Zogorski, J.S., 1999, Volatile organic compounds in untreated ambient groundwater of the United States, 1985–1995: Environmental Science & Technology, v. 33, no. 23, p. 4176–4187.

Squillace, P.J., and Price, C.V., 1996, Urban land-use study plan for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 96–217, 19 p.

Toccalino, Patricia, Nowell, L.H., Wilber, W.G., Zogorski, J.S., Donahue, Joyce, Eiden, Catherine, Krietzman, Sandra, and Post, Gloria, 2003, Development of health-based screening levels for use in State or local-scale water-quality assessments: U.S. Geological Survey Water-Resources Investigations Report 03–4054, 22 p.

U.S. Department of Commerce, 1999, Monthly station normals of temperature, precipitation, and heating and cooling degree days 1961–1990, Climatography of the United States No. 81: Asheville, N.C., National Oceanic and Atmospheric Administration, National Climatic Data Center, accessed March 13, 2005, at *ftp://ftp.ncdc.noaa.gov/pub/data/normals*

U.S. Department of Energy Information Administration, 2003, U.S. gasoline data: accessed March 20, 2003, at *http://www.eia.doe.gov/oil_gas/petroleum/info_glance/gasoline.html*

U.S. Environmental Protection Agency, 1999a, Aerobic biodegradation of organic chemicals in environmental media—A summary of field and laboratory studies: Athens, Ga., Final Report, SRC TR 99–002, 193 p. (available at *http://esc.syrres.com/demos/AERBIO.pdf*)

U.S. Environmental Protection Agency, 1999b, Anaerobic bio-degradation rates of organic chemicals in groundwater—A summary of field and laboratory studies, Appendix F—Laboratory and field studies for all compounds: Washington, D.C. (available at *http://www.epa.gov/epaoswer/hazwaste/id/hwirwste/pdf/risk/reports/s0535.pdf*).

U.S. Environmental Protection Agency, 2003a, 2001 Toxics Release Inventory Public Data Release Report: Washington, D.C., Office of Environmental Information, EPA 260–R–03–001.

U.S. Environmental Protection Agency, 2003b, Code of Federal regulations, Title 40—Protection of the Environment, Part 136 (revised July 2003).

U.S. Environmental Protection Agency, 2003c, Map of current RFG areas: accessed January 7, 2004, at *http://www.epa.gov/otaq/rfg/whereyoulive.htm*

U.S. Environmental Protection Agency, 2004a, 2004 edition of the drinking water standards and health advisories: Washington, D.C., Office of Water, EPA 822–R–04–005, 12 p.

U.S. Environmental Protection Agency, 2004b, Review of national primary drinking water regulations—Reassessment of practical quantitation limits: accessed April 28, 2004, at *http://www.epa.gov/safewater/standard/review/methods.html*

U.S. Environmental Protection Agency, 2004c, Envirofacts data warehouse: accessed April 28, 2004, at *http://www.epa.gov/enviro/*

U.S. Environmental Protection Agency, 2005a, Common chemicals found at Superfund sites: accessed January 24, 2005, at *http://www.epa.gov/superfund/resources/chemicals.htm*

U.S. Environmental Protection Agency, 2005b, Underground storage tanks sites: accessed January 24, 2005, at *http://www.epa.gov/swerust1/index.htm*

U.S. Environmental Protection Agency, 2006, Drinking water contaminant candidate list: accessed January 10, 2006, at *http://www.epa.gov/safewater/ccl/index.html*.

U.S. Geological Survey, 1990, Land use and land cover digital data from 1:250,000- and 1:100,000-scale maps—Data user guide 4: Reston, Virginia, 25 p.

Vista Information Solutions, 1999, StarView Real Estate 2.6.1. [proprietary computer software with digital data].

Vogelmann, J.E., Howard, S.M., Yang, L., Larson, C.R., Wylie, B.K., and Van Driel, N., 2001, Completion of the 1990s National Land Cover Data Set for the conterminous United States from Landsat Thematic Mapper data and ancillary data sources: Photogrammetric Engineering & Remote Sensing, v. 67, p. 650–662.

Wahl, K.L., and Wahl, T.L., 1995, Determining the flow of Comal Springs at New Braunfels, Texas, Texas Water '95, American Society of Civil Engineers, August 16–17, 1995: American Society of Civil Engineers, accessed March 25, 2003, at *http://www.usbr.gov/pmts/hydraulics_lab/twahl/bfi/texaswater95/comalsprings.html*

Wilde, F.D., Radtke, D.B., Gibs, Jacob, and Iwatsubo, R.T., 1999, Collection of water samples: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A4, accessed February 17, 2005, at *http://pubs.water.usgs.gov/twri9A4/*

Wilde, F.D., Schertz, T.L., and Radtke, D.B., 1999, Quality-control samples: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A4.3, accessed February 17, 2005, at *http://water.usgs.gov/owq/FieldManual/chapter4/html/4.3_contents.html*

Wolock, D.M., 1997, STATSGO soil characteristics for the conterminous United States: U.S. Geological Survey Open-File Report 97–656, digital data files.

Wolock, D.M., 2003, Estimated mean annual natural ground-water recharge estimates in the conterminous United States: U.S. Geological Survey Open-File Report 03–311, digital data set, accessed February 23, 2005, at *http://water.usgs.gov/lookup/getspatial?rech48grd*

Wright, Bruce; Tait, Mike; Lins, Katherine; Crawford, Janet; Benjamin, Susan; and Brown, Jesslyn, 1995, Integrating multi-source land use and land cover data: U.S. Geological Survey Open-File Report 95–652, 22 p.

Zogorski, J.S., Carter, J.M., Ivahnenko, Tamara, Lapham, W.W., Moran, M.J., Rowe, B.L., Squillace, P.J., and Toccalion, P.T., 2006, The quality of our Nation's waters—Volatile organic compounds in the Nation's ground water and drinking-water supply wells: U.S. Geological Survey Circular 1292, 101 p.