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NATIONAL WATER-QUALITY ASSESSMENT PROGRAM
NATIONAL SYNTHESIS ON VOLATILE ORGANIC COMPOUNDS

Occurrence and Implications of Selected Chlorinated Solvents in Ground Water and Source Water in the United States and in Drinking Water in 12 Northeast and Mid-Atlantic States, 1993–2002

Scientific Investigations Report 2005–5268

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

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By Michael J. Moran

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

U.S. Geological Survey
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Foreword

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

The USGS implemented the National Water-Quality Assessment (NAWQA) Program to support national, regional, and local information needs and decisions related to water-quality management and policy. Shaped by and coordinated with ongoing efforts of other Federal, State, and local agencies, the NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are the conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues. NAWQA results can contribute to informed decisions that result in practical and effective water-resource management and strategies that protect and restore water quality.

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

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

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

The NAWQA Program recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for a fully integrated understanding of watersheds and for cost-effective management, regulation, and conservation of our Nation's water resources. The Program, therefore, depends extensively on the advice, cooperation, and information from other Federal, State, interstate, Tribal, and local agencies, non-government organizations, industry, academia, and other stakeholder groups. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch
Associate Director for Water

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Acronyms Used in This Report:

AWWARF	American Water Works Association Research Foundation
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CWS	Community water system
GC/MS	Gas chromatography/mass spectrometry
MCL	Maximum Contaminant Level
MTBE	Methyl *tert*-butyl ether
MWDSC	Metropolitan Water District of Southern California
NAWQA	National Water-Quality Assessment
NWQL	National Water Quality Laboratory
PCE	Perchloroethene
RCRA	Resource Conservation and Recovery Act
SDWA	Safe Drinking Water Act
TCA	1,1,1-Trichloroethane
TCE	Trichloroethene
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

Occurrence and Implications of Selected Chlorinated Solvents in Ground Water and Source Water in the United States and in Drinking Water in 12 Northeast and Mid-Atlantic States, 1993–2002

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Abstract

The U.S. Geological Survey has collected or compiled data on select chlorinated solvents in samples of ground water, source water, and drinking water. The water samples were collected during 1993–2002. Data on solvents in ground water and source water were available for the conterminous United States, Alaska, and Hawaii. Data on solvents in drinking water only were available for 12 Northeast and Mid-Atlantic States. The occurrence and distribution of four solvents were examined—methlyene chloride, 1,1,1-trichloroethane, tetrachloroethene, and trichloroethene.

Out of 51 to 55 volatile organic compounds (VOCs) analyzed in samples, solvents were among the most frequently detected VOCs in all data sets. When data from ground water and source water were confined to 12 Northeast and Mid-Atlantic States, the detection frequencies of solvents were similar among all three data sets. Although low concentrations of solvents commonly were detected in ground water, some solvents had higher median quantified concentrations than other VOCs. Relative to other VOCs, solvents were ranked high in all data sets in terms of the frequency of concentrations higher than U.S. Environmental Protection Agency Maximum Contaminant Levels. Mixtures were a common mode of occurrence of solvents.

The probability of occurrence of solvents was most strongly related to the dissolved-oxygen content in ground water, with solvents having a higher probability of occurrence in conditions of relatively high dissolved oxygen compared to conditions of relatively low dissolved oxygen. The probability of occurrence of solvents in ground water also was strongly associated with urban land use and population density and with variables that represented the transport of solvents through the soil zone to ground water.

It is important for ground-water resource managers to understand the contamination potential posed by solvents, especially in resources that are critical as drinking-water supplies. Low-level analytical methods are most useful for determining the complete environmental distribution of solvents in ground

water. To protect ground-water resources, it is important for ground-water managers to (1) delineate the redox conditions of ground water in the aquifer in order to predict the potential fate of solvents, (2) determine and control the sources, or potential sources, of solvents to ground water, and (3) establish the susceptibility of aquifers by fully ascertaining the hydraulic properties of the saturated and vadose zones.

Introduction

Chlorinated solvents are volatile organic compounds (VOCs) that contain chlorine. In general, chlorinated solvents have low water solubilities and high volatilities and densities relative to other VOCs. They are used in a variety of commercial, industrial, manufacturing, and domestic applications. Chlorinated solvents (hereafter referred to as solvents) are used in the aerospace and electronics industries; dry cleaning; manufacture of foam; paint removal/stripping; manufacture of pharmaceuticals; metal cleaning and degreasing; and wood manufacturing (Halogenated Solvents Industry Alliance, 2004a). Solvents also can be found in a variety of household consumer products including drain, oven, and pipe cleaners; shoe polish; household degreasers; typewriter correction fluid; deodorizers; leather dyes; photographic supplies; tar remover; waxes; and pesticides (U.S. Environmental Protection Agency, 1980).

Production of solvents began in the United States in the early 20th century. Carbon tetrachloride was the first solvent produced in the United States and was the main solvent used for the first half of the 20th century. Production of trichloroethene (TCE) and perchloroethene (PCE) began in the 1920s (Pankow and Cherry, 1996). After World War II, production and usage of these two solvents in industry increased markedly, and they became the most commonly used solvents.

Two other commonly used solvents during this time period were methylene chloride and 1,1,1-trichloroethane (TCA). The production of methylene chloride, PCE, TCA, and TCE generally peaked in the 1970s and has been declining since then due mostly to the human-health and environmental concerns

associated with these compounds (Pankow and Cherry, 1996). For example, TCE has been linked to potential human-health effects including anemia, arthritis, cancer, birth defects, and damage to the liver, kidneys, immune system, and nervous system. As another example, TCA is being phased out for most uses because of its ozone depletion potential in the upper atmosphere. Under the Montreal Protocol, production of TCA for emissive uses was phased out at the end of 1995 in Europe and at the end of 1996 in the United States, Japan, and other industrialized countries (Halogenated Solvents Industry Alliance, 1994).

Although production has been declining recently, large quantities of these solvents continue to be produced and used by many commercial and industrial sectors of society. Chemicals that have large production volumes and wide usage are highly susceptible to release to the environment. Once released to the environment, solvents have a tendency for widespread ground-water contamination due to their unique combination of physical and chemical properties. Indeed, the four solvents examined here are some of the most commonly identified organic chemicals in ground water (Pankow and Cherry, 1996; Squillace and others, 2002).

The potential sources of solvents to the environment are numerous. For example, methylene chloride, PCE, and TCE are among 29 of the chemicals, metals, and other substances most commonly found at U.S. Environmental Protection Agency (USEPA) Superfund sites (U.S. Environmental Protection Agency, 2005a). Considerable quantities of solvents are released to the environment according to information in the USEPA's Toxics Release Inventory (TRI) database. The TRI provides information on the release of toxic chemicals in the United States from various manufacturing, commercial, and industrial processes. According to the TRI, during 1998–2001, total on- and off-site releases of methylene chloride, PCE, TCE, and TCA averaged about 33 million pounds, 4 million pounds, 11 million pounds, and 0.5 million pounds, respectively (U.S. Environmental Protection Agency, 2003). Despite a decline in production due to increased regulations, PCE is still the solvent of choice for 85 to 90 percent of the approximately 30,000 dry cleaners and launderers in the United States (Doherty, 2000). Releases of PCE can occur at many points during dry-cleaning operations including air emissions, spills, inadequate storage, and drain disposal of spent PCE (U.S. Environmental Protection Agency, 1995).

As mentioned, solvents have been associated with both acute and chronic human-health problems. Some are suspected human carcinogens, and USEPA has set Maximum Contaminant Levels (MCLs) for solvents in drinking water at very low concentrations. Many of the solvents have water solubilities that are high relative to their MCLs. This means that even small spills of some solvents can result in substantial ground-water contamination problems with respect to human health.

The purpose of this report is to present information on the occurrence and implications of four solvents in ground water, source water, and drinking water. The data for this report were collected or compiled by the U.S. Geological Survey's (USGS)

National Water-Quality Assessment (NAWQA) Program and other agencies. The water samples were collected during 1993–2002.

Four solvents were selected for analyses in this report—methylene chloride (also known as dichloromethane), PCE, TCA, and TCE. Many organic compounds are classified as solvents but only these four were selected because of their long histories of use and their large production and usage relative to other solvents.

The occurrence and distribution of these solvents were determined by detection frequencies, ranges of concentrations, and areal patterns of detection. Concentrations of the solvents were compared to USEPA drinking-water standards. Occurrence, distribution, and concentration information is given for three data sets: (1) ground water on a national scale, (2) source water (derived from ground water) on a national scale, and (3) drinking water from 12 Northeast and Mid-Atlantic States.

Potential anthropogenic sources of solvents to ground water are identified and the most likely sources are highlighted. Hydrogeologic and anthropogenic factors associated with the occurrence of solvents in ground water are identified. The identification of factors associated with the occurrence of solvents may aid in understanding the sources and pathways of these chemicals to ground water and the susceptibility of aquifers to contamination.

Background

The four solvents examined in this report—methylene chloride, PCE, TCA, and TCE—are members of the family of aliphatic halogenated hydrocarbons. These compounds are produced in substantial quantities, have a variety of industrial, commercial, and domestic uses, and their release to the environment has resulted in widespread contamination of ground water. The presence of solvents in ground water, especially ground water used as a source of drinking water, can pose a potential threat to human health due to the solvent's mobility, longevity, and toxicity. Table 1 presents information for the four solvents examined in this report, including chemical abstract numbers, molecular formulas, some common synonyms and abbreviations, and the abbreviation used in this report for each compound.

Physical and Chemical Properties and Environmental Behavior of Solvents

Table 2 lists selected physical and chemical properties of the four solvents. From table 2, some general observations can be made. First, the densities of all four solvents are greater than 1. This means that the pure liquid phase of each solvent has a density greater than water. If pure liquid phases of these solvents are released to the environment, they could penetrate the water table, move down through the saturated zone, and

collect in pools on top of less permeable layers. Once pooled in such a manner, the absolute removal rates from the aquifer are usually low because the solvent pool presents a very low cross section relative to ground-water flow in the aquifer (Johnson and Pankow, 1992). In this way, the pure phase of a solvent could become a long-term source of low concentrations in an aquifer and could be very difficult to remediate.

Organic chemicals that have vapor pressures greater than about 10 Pascals are considered to be volatile. All of the four solvents have vapor pressures much higher than this value (table 2) and generally higher than other commonly used VOCs like gasoline hydrocarbons. This means that the pure liquid phase of these compounds can volatilize when spilled onto a surface or exposed to the atmosphere. Although they can readily volatilize, some mass of a solvent can be transported to the water table following a release. The solvent can be transported to the water table by gaseous diffusion, downward movement of solvent dissolved in recharge water, or by gravity movement of pure solvent liquid through the vadose zone.

In environmental systems, water solubility is one of the most important chemical properties that determines the occurrence of organic chemicals in ground water. The aqueous solubilities of the four solvents are generally higher than those of other common VOCs like gasoline hydrocarbons. For example, the aqueous solubilities of three common gasoline components benzene, ethylbenzene, and toluene are approximately 1,787, 175, and 565 milligrams per liter (mg/L) at 25 degrees Celsius (°C) (Mackay and others, 1993). The solubility of benzene is higher than the solubility of any of the solvents except for methylene chloride. However, the solubilities of all four solvents except perchloroethene are higher than either toluene or ethylbenzene.

Table 1. Selected information for the four solvents examined in this report.

[C, carbon; Cl, chlorine; H, hydrogen; --, none]

Compound name	Chemical Abstract Services Registry Number	Chemical formula	Common synonyms and abbreviations	Abbreviation used in this report
Methylene chloride	75-09-2	CH_2Cl_2	Dichloromethane	--
Perchloroethene	127-18-4	$Cl_2C{=}CCl_2$	Tetrachloroethene, perchloroethylene, tetrachloroethylene, PERC, PCE	PCE
1,1,1-Trichloroethane	71-55-6	CH_3CCl_3	Methyl chloroform, MC, TCA	TCA
Trichloroethene	79-01-6	$HClC{=}CCl_2$	Trichloroethylene, TCE	TCE

Table 2. Selected physical and chemical properties of the four solvents examined in this report.

[g/cm³, grams per cubic centimeter; °C, degrees Celsius; Pa, Pascals; mg/L, milligrams per liter; m³, cubic meters]

Compound name	Molecular weight[1]	Density[2] (g/cm³ at 25°C)	Vapor pressure[2] (Pa at 25°C)	Aqueous solubility[2] (mg/L at 25°C)	Organic carbon partitioning coefficient[2] (log Koc)	Henry's Law constant[2] at 25°C (Pa-m³/ mole)	Half-life in ground water[3] (in days)
Methylene chloride	84.94	1.33	57,365	18,680	1.20	319	35
Perchloroethene	165.83	1.62	2,462	150	2.56	1,628	540
1,1,1-Trichloroethane	133.41	1.34	16,180	1,312	2.18	1,638	343
Trichloroethene	131.39	1.46	9,680	1,100	2.03	958	987

[1]From Mackay and others, 1993.

[2]Average of values from Mackay and others, 1993.

[3]Average from Howard and others, 1991.

Although the solubilities of the four solvents generally are higher than other commonly used VOCs, their absolute solubilities are low. Nonetheless, the aqueous solubilities of all the solvents examined in this report are much higher than their human-health benchmarks for drinking water. This means that even small spills of solvents have the potential to cause contamination of ground water at concentrations that could be harmful to human health.

Chemicals with high organic partitioning coefficients will adsorb strongly to soil and rock material. The organic partitioning coefficients of the solvents are relatively low (table 2) and similar to those of the gasoline hydrocarbons. This means that sorption to organic matter and clay in soils and aquifers will not substantially retard the movement of solvents through the subsurface. However, the organic carbon partitioning coefficients for both the solvents and common gasoline components are high enough to cause some retardation of their movement in the subsurface relative to the velocity of ground water.

The Henry's Law constant is the equilibrium concentration of a dissolved organic chemical in solution relative to the partial pressure of the chemical in air above the solution. At relatively low concentrations, this value represents the air-water partitioning for organic chemicals in the environment. For chemicals with Henry's Law constants greater than about 1 Pascal-cubic meter per mole (Pa-m^3/mole), partitioning from water to air is important. For all the solvents, Henry's Law constants are substantially higher than this level (table 2) indicating that partitioning from water to air can be an important process in their environmental behavior. However, once in the saturated zone, partitioning of solvent mass across the capillary fringe has been shown to be very slow (McCarthy and Johnson, 1992).

Solvents have relatively low viscosities and low interfacial tensions compared to other commonly used VOCs. Low viscosities mean that pure liquid phases of solvents can move rapidly down through the vadose zone by gravity (Pankow and Cherry, 1996). Low interfacial tensions between solvents and water allow solvents to easily enter into small fractures and pore spaces in the subsurface and provide a source for long-term, low concentration contamination of ground water. Low interfacial tension also contributes to low retention capacities of soils for solvents.

Transformation of Solvents

In ground water, solvents can be transformed through abiotic and biotic processes (Leisinger, 1996). The half-lives of the solvents in ground water are presented in table 2. These half-lives are based on scientific judgment from various biodegradation studies and screening test data and represent the total transformation rates of the compounds whether by biotic or abiotic reactions (Howard and others, 1991). With a few exceptions, the half-lives of the gasoline hydrocarbons generally are much smaller than the half-lives of the solvents. This means that the solvents transform very slowly relative to gasoline hydro-

carbons and that they could persist for long periods of time in certain ground-water systems.

For the solvents, three types of abiotic transformation processes are important—hydrolysis, reduction, and photolysis. Hydrolysis involves the reaction of a solvent with the hydroxyl ion of water and is highly dependent on pH. Hydrolysis usually produces an alcohol but in some cases non-alcohol products are formed. Transformation of solvents by hydrolysis has been documented in various laboratory and field studies (Dilling and others, 1975; Pearson and McConell, 1975; Kollig, 1993; Washington, 1995).

For solvents, reduction generally involves hydrogenolysis where chlorine is replaced by hydrogen. Higher chlorination of the molecule tends to produce higher potential energy release during reduction. Although most solvents have sufficient Gibbs free energy to undergo abiotic reduction reactions, the potential is rarely met except under very reducing conditions and not without mediation by bacteria (Pankow and Cherry, 1996).

Photolysis occurs when light strikes a chemical and converts it to a new molecule through electron distribution. In this situation, the chemical is usually oxidized. Photolysis of solvents has been demonstrated for PCE and TCE (Pearson and McConell, 1975; Haag and others, 1996).

Although the free energy of many solvents is high enough to allow abiotic reactions like hydrogenolysis to occur, the conditions necessary to undergo the reaction are rarely met, and thus, microbes mediate most transformations of solvents (Pankow and Cherry, 1996). Biotic processes for the transformation of solvents can be either aerobic or anaerobic and occur by five possible pathways: (1) through their use as a sole carbon and energy source for growth of aerobic bacteria; (2) through their use as a growth substrate for organisms that use an electron acceptor other than oxygen (nitrate respiration); (3) through their use as a growth substrate in acetogenic fermentation; (4) through co-metabolism; and (5) through their use as an electron acceptor under hypoxic conditions (reductive dechlorination) (Beek, 2001). Halogenated aliphatic organic compounds are strong oxidants, and thus anaerobic biodegradation, anaerobic co-metabolism, or their use as electron acceptors are the most common means of their transformation (Beek, 2001).

Reductive dechlorination is an important biodegradation process for the transformation of solvents (Fathepure and others, 1987; Nyer and Duffin, 1997). Reductive dechlorination requires that microbes have access to a substrate that serves as a source of carbon and energy and as an electron donor (Montoux and others, 1996). During reductive dechlorination, the solvent is used as an electron acceptor, and chlorine atoms are sequentially removed and replaced with hydrogen. An example of reductive dechlorination is shown in figure 1. In this case, PCE is transformed to TCE through reductive dechlorination using a reductive dehalogenase enzyme. Eventually, reductive dechlorination can transform PCE to ethane by sequential removal of chlorine atoms (Swindoll and Troy, 1996).
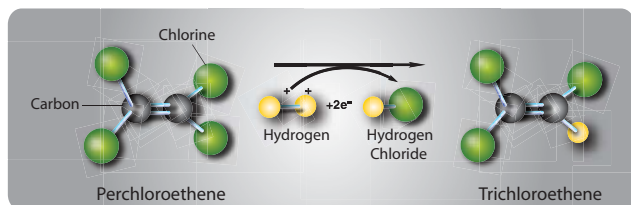
Figure 1.   Biotransformation of perchloroethene to trichloro-ethene through reductive dechlorination.

Another possible avenue for transformation of solvents is through their use as electron donors. The solvent is used as a primary substrate that supplies carbon and energy for microbes. This process usually occurs anaerobically, and microbes known to anaerobically degrade solvents include sulfate-reducing and methanogenic bacteria that use sulfate and carbon dioxide as electron acceptors (Chu and Alvarez-Cohen, 1995; van Eekert and Schraa, 2001). In some cases microbes can utilize less chlorinated compounds (such as chloroethene) aerobically with oxygen as an electron acceptor and the compound as the primary substrate (Davis and Carpenter, 1990). Although this process has been demonstrated in the laboratory for smaller molecules, the importance of this metabolic pathway for larger molecules is uncertain.

Aerobic biodegradation of solvents generally occurs through co-metabolism (Bielefeldt and others, 1995; Munkata-Marr and others, 1996). Co-metabolism is the process whereby solvents are fortuitously degraded as microbes consume other organic substrates. Although the solvents are transformed in the respiration process, the microbes do not derive any direct benefit from the transformations (Swindoll and Troy, 1996). Only a small number of organic compounds have been identified as serving as suitable primary substrates in which the co-metabolism of solvents can occur.

Some potential transformation products of solvents in water are shown in table 3. In some cases, especially for more highly chlorinated molecules, the degradation of a solvent results in a metabolite that also is a solvent. This usually occurs during reductive dechlorination that proceeds with a sequential dechlorination of highly chlorinated molecules to less chlorinated molecules. However, the specific transformation products formed during reductive dechlorination are a result of both the mechanism of degradation and the type of electron acceptors that are available (Swindoll and Troy, 1996; Nyer and Duffin, 1997).

Production and Usage of Solvents

Figure 2 shows the production of the four solvents from 1960 to 1998, in millions of kilograms. For the most part, production of each of the solvents has decreased since about 1970 or 1980. Figure 2 only shows production of these solvents in the United States, and these values do not necessarily indicate usage of solvents in the United States because substantial amounts of some solvents are exported. In addition, production may not accurately indicate usage because substantial amounts of solvents are recycled in some commercial/industrial processes. For example, most dry-cleaning equipment recycles 95 to 99 percent of the PCE used in the dry-cleaning process (Doherty, 2000).

Methylene Chloride

Methylene chloride is used widely as a chemical solvent and replaced more flammable solvents more than 60 years ago. It is commonly used in paint removers and industrial adhesive formulas. It also is used in the production of flexible urethane foams, pharmaceutical products, as a cleaning agent for fabricated metal parts, in the production of thermoplastics, in nonflammable adhesive formulations for industrial applications, and as an extraction solvent (Halogenated Solvents Industry Alliance, 2003). The largest use of methylene chloride is in paint-removal formulations. Methylene chloride also is commonly used as an extractant in the recovery and purification of a wide variety of materials including oils, fats, and waxes, and the decaffeination of coffee and tea, oleoresin extraction from a variety of spices, and for the extraction of hops (Halogenated Solvents Industry Alliance, 2003). Methylene chloride also can be found in a wide variety of commercial and consumer products such as spot removers, wood floor and panel cleaners, contact cement, super glues, spray adhesives, adhesive removers, silicone lubricants, specialized electronic cleaners, wood stains, varnishes and finishes, paint thinners, paint removers, aerosol spray paints, primers, aerosol rust removers, outdoor water repellents, glass frosting/artificial snow, spray lubricant for cars, transmission cleaners, battery terminal protectors, brake quieter/cleaner, and gasket removers (U.S. Department of Health and Human Services, 2005).

Since 1985, the production of methylene chloride has declined, in part, due to the increase in the manufacture of solvent systems that do not use methylene chloride (U.S. Department of Health and Human Services, 2005). In the United States in 2000, the demand for methylene chloride was estimated at about 91 million kilograms (Halogenated Solvents Industry Alliance, 2003). In 2000, approximately 15 million kilograms of methylene chloride were imported and approximately 57 million kilograms were exported (U.S. Department of Health and Human Services, 2005).

Perchloroethene

In the late 1940s, PCE began replacing petroleum derivatives as the main solvent used in dry cleaning (Halogenated Solvents Industry Alliance, 2005). By the early 1960s, PCE had become the most widely used dry-cleaning solvent in the United States (State Coalition for Remediation of Drycleaners, 2002). However, during the 1990s its use in dry cleaning declined in order to meet more stringent government regulations for workplace exposure (U.S. Department of Health and Human Services, 2005). Nonetheless, as of 2002, PCE was still used as the primary cleaning solvent in about 85 percent of professional dry cleaners (Sinsheimer and others, 2002).

Table 3. Possible transformation products of the four solvents examined in this report.

[PCE, perchloroethene; TCA, 1,1,1-trichoroethane; TCE, trichloroethene; CO_2, carbon dioxide; CO, carbon monoxide]

Parent compound	Possible transformation product in water	References
Methylene chloride	chloromethane	Swindoll and Troy, 1996
	methane	Swindoll and Troy, 1996
	formaldehyde	Dilling and others, 1975; Belkin, 1992; Kollig, 1993; Washington, 1995
	formic acid	Dilling and others, 1975
	hydrogen chloride	Dilling and others, 1975; Kollig, 1993
	methanol	Dilling and others, 1975
	CO_2	Swindoll and Troy, 1996
	CO	Dilling and others, 1975
PCE	TCE	Parsons and others, 1985; Fathepure and others, 1987; van der Meer and others, 1992
	trans-1,2-dichloroethene	Parsons and others, 1985; van Eekert and Schraa, 2001
	cis-1,2-dichloroethene	Parsons and others, 1985; van der Meer and others, 1992
	1,1-dichloroethene	Swindoll and Troy, 1996; van Eekert and Schraa, 2001
	vinyl chloride	Parsons and others, 1985; van der Meer and others, 1992
	1,2-dichloroethane	Swindoll and Troy, 1996
	chloroethane	Swindoll and Troy, 1996
	ethene	Swindoll and Troy, 1996; van Eekert and Schraa, 2001
	ethane	van der Meer and others, 1992
	trichloroacetic acid	Dilling and others, 1975
	hydrochloric acid	Dilling and others, 1975
	CO_2	Swindoll and Troy, 1996
TCA	1,1-dichloroethane	Parsons and others, 1985; Criddle and McCarty, 1991; Semprini and others, 1992
	1,1-dichloroethene	Dilling and others, 1975; Kollig, 1993; McNab and Narasimhan, 1994
	chloroethane	Semprini and others, 1992
	chloroethanol	Swindoll and Troy, 1996
	ethane	Swindoll and Troy, 1996
	formaldehyde	Swindoll and Troy, 1996
	acetic acid	Criddle and McCarty, 1991; Semprini and others, 1992; Washington, 1995
	hydrochloric acid	Washington, 1995
	CO_2	Swindoll and Troy, 1996
TCE	*trans*-1,2-dichloroethene	Kloepfer and others, 1985; Barrio-Lage and others, 1986; Wilson and others, 1986
	cis-1,2-dichloroethene	Barrio-Lage and others, 1986; Barrio-Lage and others, 1987
	1,1-dichloroethene	Fliermans and others, 1988
	vinyl chloride	Barrio-Lage and others, 1986; Wilson and others, 1986
	1,2-dichloroethane	Swindoll and Troy, 1996
	trichloromethane	Fliermans and others, 1988
	chloroethane	Swindoll and Troy, 1996
	ethene	Swindoll and Troy, 1996
	ethane	Swindoll and Troy, 1996
	trichloroethene oxide	Belkin, 1992
	dichloroacetic acid	Dilling and others, 1975; Alvarez-Cohen and McCarty, 1991
	hydrogen chloride	Dilling and others, 1975
	hydrochloric acid	Fliermans and others, 1988
	cis-dihydrodiol	Nelson and others, 1988
	3-methylcatechol	Nelson and others, 1988
	2,2,2-trichloroacetaldehyde	Alvarez-Cohen and McCarty, 1991
	glyoxylic acid	Alvarez-Cohen and McCarty, 1991
	formic acid	Alvarez-Cohen and McCarty, 1991
	CO_2	Swindoll and Troy, 1996
	CO	Alvarez-Cohen and McCarty, 1991
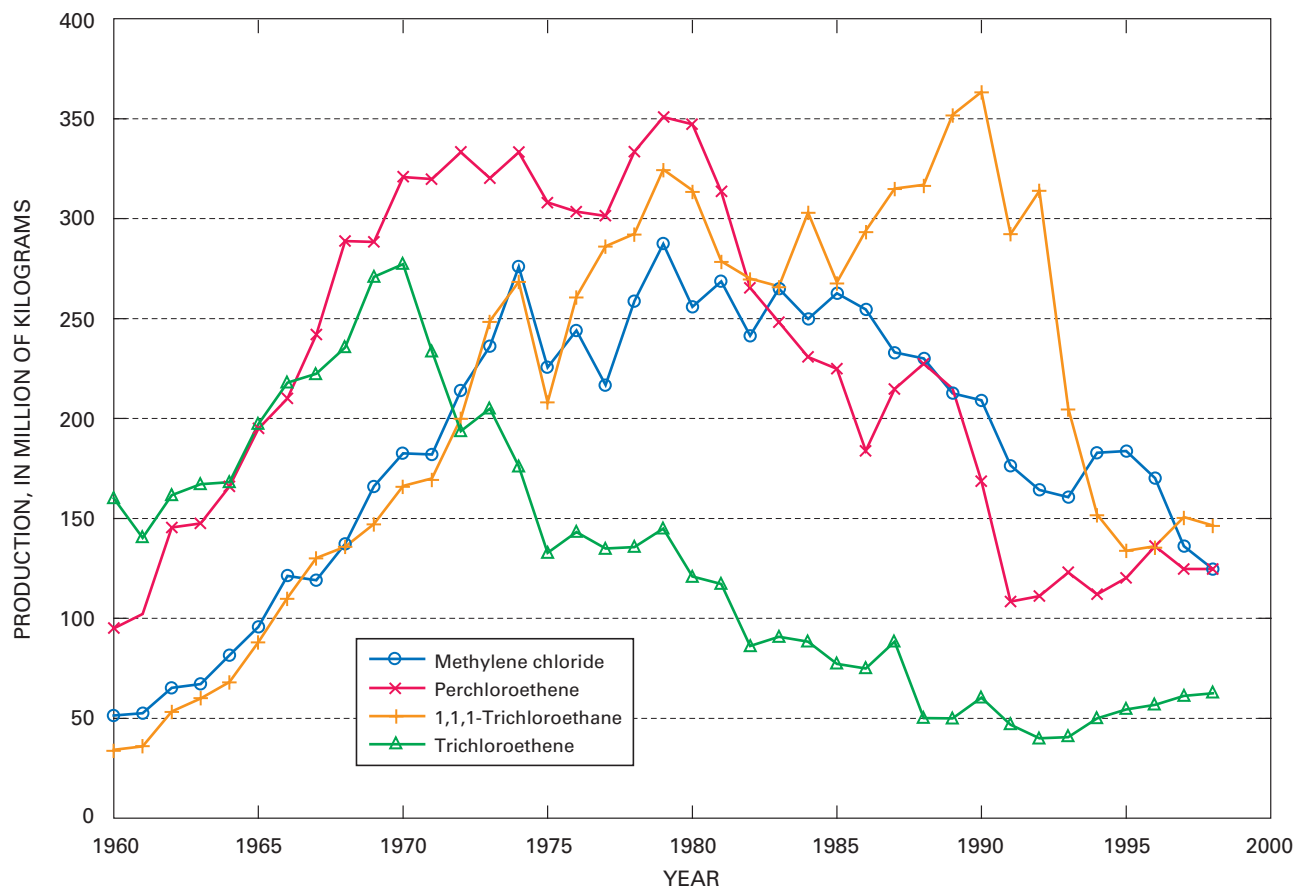
Figure 2. Production of four solvents in the United States from 1960–1998 (Pankow and Cherry, 1996; Chemical Manufacturers Association, 1997, 1998).

In 1998, the majority of PCE used in the United States (about 50 percent) was used as a chemical intermediate in the manufacture of several hydrofluorocarbons that are alternatives to chlorofluorocarbon refrigerants. About 25 percent was used in dry cleaning and textile processing. The remainder was used in automotive aerosols, metal cleaning and degreasing, and miscellaneous uses (Halogenated Solvents Industry Alliance, 2005). PCE can be found in a variety of commercial and consumer products such as insulating fluid and cooling gas in electrical transformers, paint removers, printing inks, art supplies, adhesive formulations, paper coatings, leather treatments, water repellents, automotive cleaners, silicone lubricants, spot removers, as a pesticide intermediate, and as an extractant for pharmaceuticals (U.S. Department of Health and Human Services, 2005; Halogenated Solvents Industry Alliance, 2005).

Production of PCE in the United States declined more than 60 percent from 1980 to 1993 (fig. 2) because of increased solvent recycling and increased occupational exposure regulations (U.S. Department of Health and Human Services, 2005; Halogenated Solvents Industry Alliance, 2005). However, in

recent years the demand for PCE has increased slightly from about 112 million kilograms in 1996 to about 125 million kilograms in 1999 (fig. 2). According to the U.S Department of Health and Human Services (2005), three companies in the United States produced PCE as of 2005, with a combined capacity of about 160 million kilograms. From 1998 to 2001, the United States imported about 16 million kilograms of PCE per year and exported about 27 million kilograms per year (U.S. Department of Health and Human Services, 2005).

1,1,1-Trichloroethane

Beginning in the mid-1950s, TCA was used as a cold cleaning solvent substitute for carbon tetrachloride. TCA is used mainly for vapor degreasing and cold cleaning of fabricated metal parts and other materials. TCA also is used in fluoropolymer synthesis, as a solvent in adhesive and aerosol formulations, for the production of certain coatings and inks, for a variety of textile applications, for cleaning motion picture film, and for dry cleaning leather and suede garments (Halogenated Solvents Industry Alliance, 1994). TCA can also be found

in a variety of commercial and consumer products such as aerosol formulations, adhesives, protective surface coatings, cutting oils, and printing inks (U.S. Environmental Protection Agency, 2000a).

Because of concerns about ozone depletion, the USEPA has restricted future production of TCA in the United States. Under the Montreal Protocol on Substances That Deplete the Ozone Layer, as amended in June 1990 and November 1992, and under Title VI of the Clean Air Act, the use of TCA is being phased out (Halogenated Solvents Industry Alliance, 1994). Under Title VI of the Clean Air Act, restrictions on the uses of TCA were imposed and labeling was required for certain products containing or made with TCA. Pursuant to the Clean Air Act, the USEPA accelerated a phase-out in the production and import of TCA allowing only essential uses of the compound after 1996 (U.S. Environmental Protection Agency, 1993). Although use of TCA is being phased out, sources indicate that relatively large quantities of TCA were still being produced in the United States after this date, with 151 and 147 million kilograms of TCA produced in 1997 and 1998 (fig. 2). Under the Clean Air Act, TCA may be produced domestically for export (Agency for Toxic Substances and Disease Registry, 2004).

Trichloroethene

TCE is used mainly as a chemical intermediate in the production of hydroflurocarbon refrigerants and as a metal cleaning agent (Halogenated Solvents Industry Alliance, 2001). TCE is especially valuable as a metal degreaser because of its cleaning properties, low flammability, and lack of a measurable flashpoint. Four main industries use TCE in vapor or cold degreasing operations—furniture and fixtures, fabricated metal products, electrical and electronic equipment, and transport equipment (U.S. Department of Health and Human Services, 2005). TCE also is used as a chemical process intermediate in fluorochemical and polyvinyl chloride production. In 1999, more than 50 percent of TCE was used as a chemical intermediate, 42 percent was used in metal degreasing and cleaning, and the remainder was used for miscellaneous purposes (Halogenated Solvents Industry Alliance, 2001). TCE also can be found in a variety of commercial and consumer products such as adhesives, lubricants, paints, varnishes, paint strippers, pesticides, and cold metal cleaners (U.S. Department of Health and Human Services, 2005).

Production of TCE declined by almost 80 percent from 1970 to 1990 (fig. 2). This decline is most likely due to the human-health concerns associated with the use of TCE. In 1998, U.S. demand for TCE was about 78 million kilograms, of which about 7 million kilograms were imported. In 1998, about 38 million kilograms of TCE were exported (Halogenated Solvents Industry Alliance, 2001).

Health Effects of Solvents

Solvents have been associated with both acute and chronic human-health problems. Acute health problems are those that reach a critical point in a relatively short period of time. Chronic health problems are those that occur over a lengthy period of time and include both cancer and noncancer effects. The health effects of solvents can be different depending on the route of exposure. There are numerous exposure routes for solvents in the human body. For solvents in ground water, exposure occurs mainly through drinking water containing solvents and through breathing solvents that have been transferred from water to air. Solvents can get into air by volatilization from contaminated drinking water in showers or taps.

Although a large amount of data indicates negative health effects from exposure to solvents, not all data indicate a negative health effect. In 1992, concentrations of as much as 212 micrograms per liter (µg/L) of TCE and 180 µg/L of PCE were found in the drinking water of two villages in Finland. Even though the time of exposure may have been as long as several decades for some people, no increased incidence rates of total cancer, liver cancer, non-Hodgkin's lymphoma, Hodgkin's disease, multiple myeloma, or leukemia were observed in the exposed population. The contaminants appeared to be metabolized by exposed individuals and excreted as dichloroacetic or trichloroacetic acid (Vartiainen and others, 1993).

Methylene Chloride

The effects of acute inhalation of methylene chloride in humans include decreased visual, auditory, and psychomotor functions and effects on the central nervous system, but these effects are reversible once exposure ceases. Tests involving acute exposure of animals to methylene chloride have shown moderate acute toxicity from oral exposure (Agency for Toxic Substances and Disease Registry, 2000). The major effects from chronic inhalation exposure to methylene chloride in humans are effects on the central nervous system, headaches, dizziness, nausea, and memory loss. Animal studies indicate that the inhalation of methylene chloride causes effects on the liver, kidney, central nervous system, and cardiovascular system (Agency for Toxic Substances and Disease Registry, 2000).

Animal studies have demonstrated that methylene chloride crosses the placental barrier, and minor skeletal variations and lowered fetal body weights have been noted. No studies have indicated developmental or reproductive effects in humans from inhalation or oral exposure (Agency for Toxic Substances and Disease Registry, 2000).

According to the U.S. Department of Health and Human Services (2005) in its eleventh annual report on carcinogens, methylene chloride is reasonably anticipated to be a human carcinogen based on sufficient evidence of carcinogenicity in experimental animals. The USEPA has set an MCL in drinking

water of 5 µg/L for methylene chloride to be protective of both cancer and noncancer health effects. The USEPA also classifies methylene chloride as a group B2 carcinogen (probable human carcinogen), indicating that sufficient evidence in animals exists to classify it as a carcinogen but evidence in humans is lacking (U.S. Environmental Protection Agency, 2004a). The USEPA is currently reassessing the human-health effects of methylene chloride but the study will not be completed until 2006 or later (U.S. Environmental Protection Agency, 2005b).

Perchloroethene

The effects of acute inhalation of PCE in humans include irritation of the upper respiratory tract and eyes, kidney dysfunction, and at lower concentrations, neurological effects such as reversible mood and behavioral changes, impairment of coordination, dizziness, headache, sleepiness, and unconsciousness. However, mice exposed acutely to PCE from oral routes indicated low toxicity. The major noncancer effects from chronic inhalation exposure to PCE in humans include neurological effects, such as sensory symptoms and headaches, impairments in cognitive and motor neurobehavioral functioning, color vision decrements, cardiac arrhythmia, liver damage, and possible kidney effects (Agency for Toxic Substances and Disease Registry, 1997a).

Some adverse reproductive effects, such as spontaneous abortions, menstrual disorders, altered sperm structure, and reduced fertility, have been reported in studies of workers occupationally exposed to inhalation of PCE. However, no definitive conclusions can be made because of the limitations of the studies (Agency for Toxic Substances and Disease Registry, 1997a). In one study of residents exposed to drinking water contaminated with PCE and other solvents, there was an indication that birth defects were associated with exposure. However, no firm conclusions can be drawn from this study due to multiple chemical exposures and problems with the analysis (Agency for Toxic Substances and Disease Registry, 1997a).

According to the U.S. Department of Health and Human Services (2005) in its eleventh annual report on carcinogens, PCE is reasonably anticipated to be a human carcinogen based on sufficient evidence of carcinogenicity in experimental animals. Epidemiological studies of dry-cleaning workers exposed to PCE and other solvents indicate an increased risk for a variety of cancers. However, these studies were complicated by confounding factors such as lifestyles of the participants (Agency for Toxic Substances and Disease Registry, 1997a). In animal studies, an increased incidence of liver tumors in mice from inhalation and gavage exposure to PCE has been reported. An increased rate of kidney and mononuclear cell leukemia in rats through inhalation exposure also has been reported (U.S. Environmental Protection Agency, 1988, 2000b; Agency for Toxic Substances and Disease Registry, 1997a). One study involving humans reported that there was a potential association between drinking water contaminated with PCE and an increased risk of childhood leukemia. However, the statistical

significance of the incidence of leukemia has not been resolved (Agency for Toxic Substances and Disease Registry, 1997a).

The USEPA has set an MCL in drinking water of 5 µg/L for PCE to be protective of both cancer and noncancer health effects (U.S. Environmental Protection Agency, 2004a). As of 2004, the USEPA does not have a classification for the carcinogenicity of PCE (U.S. Environmental Protection Agency, 2004a). However, the USEPA's Science Advisory Board placed PCE on a continuum between probable human carcinogen (B2) and possible human carcinogen (C). The International Agency for Research on Cancer also has classified PCE as a probable human carcinogen (Agency for Toxic Substances and Disease Registry, 1997a). The USEPA is currently reassessing the human-health effects of PCE but the study will not be completed until 2006 or later (U.S. Environmental Protection Agency, 2005b).

1,1,1-Trichloroethane

The effects of acute inhalation of TCA in humans include mild hepatic effects, mild motor impairment (for example, increased reaction time), lightheadedness, impaired balance, dizziness, nausea, vomiting, diarrhea, loss of consciousness, decreased blood pressure, and ataxia. Cardiac arrhythmia and respiratory arrest may result from the depression of the central nervous system (Agency for Toxic Substances and Disease Registry, 2004). Tests involving acute exposure of rats, mice, rabbits, and guinea pigs have demonstrated that TCA has a low acute toxicity from oral exposure. Most studies have not reported adverse effects from chronic oral or inhalation exposure to low levels of TCA in humans or animals (Agency for Toxic Substances and Disease Registry, 2004). Some liver damage and neurological effects have been observed in rodents chronically exposed to TCA by inhalation (U.S. Environmental Protection Agency, 2000a).

Epidemiologic studies have found no relation between adverse pregnancy outcomes and exposure of mothers or fathers to TCA. Animal studies have not reported developmental or reproductive effects from exposure to TCA (Agency for Toxic Substances and Disease Registry, 2004).

Information is not available on the carcinogenic effects of TCA in humans. Two animal studies have not demonstrated carcinogenicity from oral or inhalation exposure to TCA; however, the data are considered to be inadequate (U.S. Environmental Protection Agency, 2000a). The USEPA has set an MCL in drinking water of 200 µg/L for TCA to be protective of both cancer and noncancer health effects. The USEPA classifies TCA as a group D carcinogen based on no reported human data and inadequate animal data (U.S. Environmental Protection Agency, 2004a). This indicates that the chemical is not classifiable as to its human carcinogenicity. The USEPA is currently reassessing the human-health effects of TCA but the study will not be completed until 2006 or later (U.S. Environmental Protection Agency, 2005b).

Trichloroethene

Acute inhalation of TCE in humans primarily produces effects on the central nervous systems with symptoms such as sleepiness, fatigue, headache, confusion, and feelings of euphoria. Effects on the liver, kidneys, gastrointestinal system, and skin also have been noted. Tests involving acute exposure of rats and mice have shown TCE to have moderate toxicity from oral exposure. The major noncancer effects from chronic inhalation exposure to TCE in humans include dizziness, headache, sleepiness, nausea, confusion, blurred vision, facial numbness, and weakness (Agency for Toxic Substances and Disease Registry, 1997b). Effects to the liver, kidneys, and immune and endocrine systems also have been seen in humans occupationally exposed to inhalation of TCE or from contaminated drinking water (U.S. Environmental Protection Agency, 2001).

Some studies have indicated reproductive or developmental effects from exposure to TCE (U.S. Environmental Protection Agency, 2000c). Studies of women occupationally and non-occupationally exposed to inhalation of TCE have reported increases in the incidence of miscarriages. The presence of other chemicals, however, limits the ability to draw conclusions specific to TCE. Studies involving animals have indicated developmental effects from exposure to TCE and its metabolites (U.S. Environmental Protection Agency, 2000c). Also, several studies have shown associations between the occurrence of TCE and PCE in drinking water and small birth weights in babies (Sonnenfeld and others, 2001; Rodenbeck and others, 2000).

According to the U.S. Department of Health and Human Services (2005) in its eleventh annual report on carcinogens, TCE is reasonably anticipated to be a human carcinogen based on limited human studies and sufficient evidence of carcinogenicity in experimental animals. An analysis of available epidemiological studies reports TCE exposure to be associated with several types of cancers in humans, especially kidney, liver, cervix, and lymphatic system (U.S. Environmental Protection Agency, 2001). These results are supported by recent molecular epidemiology studies showing specific renal cell mutations found primarily in renal cell carcinoma patients exposed to TCE. Animal studies have reported increases in lung, liver, kidney, and testicular tumors and lymphoma from inhalation and oral exposures to TCE in rats and mice (Agency for Toxic Substances and Disease Registry, 1997b).

The USEPA has set an MCL in drinking water of 5 μg/L for TCE to be protective of both cancer and noncancer health effects. The USEPA classifies TCE as a group B2 carcinogen (probable human carcinogen), indicating that sufficient evidence in animals exists to classify it as a carcinogen but evidence in humans is lacking (U.S. Environmental Protection Agency, 2004a). The USEPA currently is reassessing the human-health effects of TCE but the study will not be completed until 2006 or later (U.S. Environmental Protection Agency, 2005b).

Potential Sources of Solvents to Ground Water

There are numerous potential sources of solvents to ground water. Solvents in ground water can have two distinct sources—anthropogenic and natural. Anthropogenic sources of solvents are defined in this report as sources that ultimately have a human origin. For example, PCE released from a leaking underground storage tank (UST) and transported to ground water by gravitational flow would be considered to be an anthropogenic source of PCE. Although anthropogenic sources generally are the focus of most ground-water quality assessments, a fraction of the concentrations of solvents in ground water in some areas may have natural origins. Natural sources of solvents are defined in this report as sources that do not have a human origin. For example, methylene chloride that was formed in pine needles, leached from them, and transported to ground water through recharge would be considered a natural source.

It may be possible, through isotopic fractionation, to identify the component of solvents in ground water in some areas that may originate from anthropogenic sources compared to natural sources. However, separating the anthropogenic and natural components of solvent concentrations in ground water has not yet been attempted and would likely be difficult to achieve. Nonetheless, it is still useful to examine some of the possible anthropogenic and natural sources of solvents to ground water.

Anthropogenic Sources

A wide variety of anthropogenic sources can contribute solvents to ground water. Some commercial and industrial activities use solvents in large quantities and could be direct sources of solvents to ground water. These activities include chemical manufacturing, cold cleaning, metal degreasing/cleaning, dry cleaning, textile production, paint removal/stripping, electronics and pharmaceutical manufacturing, and aerospace industries. In addition, small businesses in nearly every community use solvents in many activities including dry cleaning, machine cleaning, photographic processing, and printing.

Solvents can be released to the environment in many different ways and in either concentrated (point source) or dispersed (nonpoint source) discharges. Potential sources of concentrated discharges include leaks from underground or aboveground tanks used for storing solvents or hazardous waste containing solvents; leaks from chemicals drums or other smaller storage containers; leaks from distribution pipelines; spills at bulk loading or unloading facilities; spills from truck or rail transport; intentional disposal of waste materials; leaks from municipal landfills, settling ponds, or lagoons; leaks from hazardous waste storage, treatment, or disposal facilities; and large consumer releases of solvent-containing products or wastes. Disposal of some solvent-containing waste may have occurred in the past in underground injection wells. This waste

could then act as a concentrated source of solvents to ground water. However, underground disposal of waste containing any of the four solvents examined in this report was prohibited in 1990 (U.S. Environmental Protection Agency, 2002).

Potential sources of dispersed discharges include leaks or releases from domestic septic systems; leaks from domestic waste disposal facilities; evaporative losses from storage tanks, transport pipelines, or transfer processes; land farming of contaminated waste or sludges; evaporative losses from manu-facturing or cleaning processes; runoff from agricultural areas where solvents have been applied (such as adjuvants in pesti-cides) or deposited from air; releases from dry wells or drainage tiles; partitioning from air and wet deposition; and small consumer releases of solvent-containing products or wastes.

Natural Sources

Few natural sources have been identified for the four solvents examined here. Sinkkonen and others (1995) found concentrations of methylene chloride and PCE in samples of pine needles from an area in southern Finland near a metal scrap plant. However, the origin of the solvents was not clear. It is possible that the solvents were bio-accumulated by the trees from contaminated air or water at the site. In this case, the origin of the solvents would be anthropogenic and not natural. On the other hand, some or all of the concentrations could have been produced naturally by the trees.

Laturnus and others (2000) found TCE, PCE, and TCA in ambient air and soil air in a spruce forest in Denmark. In ground water in the same area, chloroform, PCE, and TCE frequently were detected. However, only the concentrations of chloroform were presumed to have a possible natural source. The authors concluded that the concentrations of PCE and TCE in ground water and TCA in air were consistent with global background air concentrations from anthropogenic sources.

Both TCE and PCE are produced by several temperate and subtropical species of marine microalgae (Abrahamsson and others, 1995). It has been concluded that the emission of these compounds by these algae is of such a magnitude that it should be considered in a global atmospheric chlorine budget. However, it is not clear if production of these compounds by marine algae has resulted in measurable concentrations of TCE or PCE in terrestrial ground water, although ground water in proximity to marine environments might be affected.

Haloalkanes like methylene chloride sometimes can be trapped in rocks. When the rocks are crushed during mining operations or weathering processes, small concentrations of some of these compounds can be released (Isidorov and others, 1993). Methylene chloride, TCE, and PCE also have been detected in gas emissions from volcanoes around the world (Jordan and others, 2000). In some cases, the concentrations of these solvents were higher than their background atmospheric concentrations. Nonetheless, the water equilibrium concentra-tions were still quite low being on the order of 10^{-4} to 10^{-1} μg/L.

Thus, some measurable concentrations of these solvents in ground water could occur in the vicinity of volcanic emissions; however, the concentrations in ground water likely would decrease quickly away from the volcanic source.

Data and Methods

A variety of data sources, analysis methods, and statistical tests were used in this analysis of solvents. Much of the data used in this analysis came from the USGS NAWQA Program. Local water-quality assessments that included analyses for solvents formed the basis of the NAWQA Program and these areas were known as Study Units. Data on solvents as collected or compiled by the Study Units were then aggregated and analyzed on a comprehensive national basis. Data on solvents also were collected from a study of source water for community water systems (CWSs) located throughout the United States. Finally, data were compiled on solvents in drinking water from CWSs in 12 Northeast and Mid-Atlantic States.

Solvent Data Sets

The concentration data for solvents came from three sources: (1) the NAWQA Program that collected or compiled data from ground water throughout the United States from 1993–2002, (2) a collaborative effort of the NAWQA Program and other organizations that sampled ground water used by CWSs as a source of drinking water (prior to treatment, if any) throughout the United States from 1999–2000, and (3) the NAWQA Program that compiled data on drinking water from CWSs in 12 Northeast and Mid-Atlantic States that were sampled from 1993–1998. For ease of understanding, the data from the NAWQA studies (source 1) will be referred to as ground water; the data from the source-water survey (source 2) will be referred to as source water; and the data from the drinking-water survey (source 3) will be referred to as drinking water.

Ground-Water Data

Data on solvents in ground water came from the NAWQA Program. The primary goals of NAWQA during its first decade of sampling (Cycle 1) were (1) to provide a nationally consis-tent description of current water-quality conditions for a large part of the Nation's water resources; (2) to define long-term trends in water quality; and (3) to identify, describe, and explain, as possible, the major factors that affect water-quality conditions and trends.

Major elements of the design of ground-water quality sampling in Cycle 1 were aquifer and shallow ground-water studies (Gilliom and others, 1995). NAWQA conducted three types of studies in Cycle 1 that can be summarized as follows:

1. Aquifer Studies—These studies were broad assessments of the occurrence and distribution of contaminants in aquifers used for drinking-water supply. Originally called Study-Unit Surveys (Gilliom and others, 1995) and also called Major Aquifer Surveys, these studies sampled large areal and depth dimensions of the aquifer of interest. The potential sampling area was the extent of the aquifer, regardless of land use. Some existing network-based water-quality data, collected by other agencies, also were compiled. These data collected by other agencies are referred to as retrospective data and are considered to be very similar to NAWQA aquifer studies and have the same design characteristics and data-collection objectives (Lapham and Tadayon, 1996).

2. Shallow Ground-Water Studies in Urban Areas—These studies were assessments of the occurrence and distribution of contaminants in shallow ground water under large (population greater than 250,000) metropolitan areas. Originally classified as Land-Use Studies (Gilliom and others, 1995), the purpose of these studies was to define the quality of shallow ground water in urban land-use areas. Another important purpose of these studies was to determine which anthropogenic and natural factors most strongly affect the occurrence of contaminants in these shallow aquifers. In some cases, the focus was on recently recharged ground water in shallow aquifers underlying new residential/commercial regions (Squillace and Price, 1996). For studies in new residential/commercial areas, at least 75 percent of a 500-meter (m) radial area around the well was required to be within an area of land use classified as new residential/commercial (Squillace and Price, 1996).

3. Shallow Ground-Water Studies in Agricultural Areas—These studies were assessments of the occurrence and distribution of contaminants in shallow ground water underlying agricultural areas. Originally classified as Land-Use Studies (Gilliom and others, 1995), the purpose of these studies was to define ground-water quality in recharge areas of shallow aquifers underlying a specific agricultural setting and to determine which anthropogenic and natural factors most strongly affect the occurrence of contaminants in these shallow aquifers (Gilliom and others, 1995).

Data from all three studies are included in this report as ground water. In some cases, results are given for ground water as a whole and sometimes by study. Identification of sampling sites in aquifer studies did not focus on a specific land use around the well. Thus, ground water sampled in the aquifer studies underlies a mixture of urban, agricultural, and other land uses and is hereafter referred to as a mixed land-use setting.

The characterization of water quality in each of the three studies generally was achieved by sampling 20 to 30 spatially distributed, randomly selected wells throughout each aquifer or shallow ground-water area of interest. For aquifer studies, existing wells were sampled to achieve a preliminary assessment (Gilliom and others, 1995). Domestic wells were selected preferentially over other types of wells, if available. Domestic wells were chosen because in most areas their distribution best fit the study objective of assessing the ground-water quality of aquifers using randomly selected and spatially distributed sampling points. Also, existing wells were preferred over installation of new monitoring wells because of the high costs involved in installing thousands of wells.

For shallow ground-water studies, however, many wells were installed by the NAWQA Program in order to meet the criteria for sampling the uppermost part of the ground-water system using low capacity or observation wells. In situations where new wells could not be installed, existing wells were sampled in shallow ground-water studies. In general, the wells sampled by NAWQA were not located in proximity to known point-source releases of solvents.

Ground-water samples collected from a total of 3,883 wells in NAWQA aquifer or shallow ground-water studies were analyzed for one or more of the four solvents. The number of samples of ground water available for each solvent was as follows: methylene chloride, 3,877; PCE , 3,811; TCA, 3,883; and TCE, 3,879.

For ground water sampled by NAWQA, only one sample from each well was analyzed. The sample analyzed represented the first environmental sample collected from each well. Although some wells were re-sampled for analysis of trends in water quality, only one sample was included in this report because the goal was to provide a decadal assessment of ground-water quality without regard to temporal variations. If more than one environmental sample from a well was available, the sample collected most recently was selected. NAWQA sampled many different types of wells in its studies of VOCs in ground water. Although NAWQA occasionally sampled nested wells in special studies, no data from nested wells were used in this analysis. Thus, each well represents a distinct geographic site.

Because only one sample from each well was analyzed, the term sample, as used here, is synonymous with well. For various reasons, concentration information is not available for every solvent in every sample. The numbers of samples that have concentration results for each solvent in each NAWQA study type, by well type, are given in table 4.

Discussion of USGS field and laboratory procedures including sampling and handling, and laboratory analytical methods can be found in Moran and others (in press). All samples collected for NAWQA studies were analyzed at the USGS National Water Quality Laboratory (NWQL) near Denver, Colorado. Ground-water samples analyzed by the NWQL were quantified using gas chromatography/mass spectrometry (GC/MS). Methods of analysis used by the NWQL are described in Rose and Schroeder (1995) and Connor and others (1998).

Table 4. Number of ground-water samples with concentration results for solvents by study type and well type for National Water-Quality Assessment data.

[PCE, perchloroethene; TCA, 1,1,1-trichloroethane; TCE, trichloroethene]

Well type	Methylene chloride	PCE	TCA	TCE
Aquifer studies				
Public	321	320	321	321
Domestic	1,620	1,591	1,621	1,620
Monitoring	135	119	136	136
Other	234	234	235	235
Total	2,310	2,264	2,313	2,312
Shallow ground-water studies in urban areas				
Public	7	7	7	7
Domestic	16	16	16	16
Monitoring	765	752	767	767
Other	56	57	57	57
Total	844	832	847	847
Shallow ground-water studies in agricultural areas				
Public	1	1	1	1
Domestic	247	247	247	247
Monitoring	438	430	438	435
Other	37	37	37	37
Total	723	715	723	720
Grand total	3,877	3,811	3,883	3,879

Samples collected by NAWQA were analyzed for as many as 86 different VOCs (Connor and others, 1998); however, only 55 of these VOCs were included in NAWQA's national assessment of VOCs (Bender and others, 1999). The four solvents examined in this report are among these 55 VOCs. The list of 55 VOCs and the rationale and procedures for their selection can be found in Bender and others (1999).

A variety of quality control (QC) samples were collected during NAWQA sampling. The types of QC samples collected and their purpose are outlined in Moran and others (in press). The results of the QC samples were analyzed to determine if systematic contamination of environmental samples was indicated. If systematic contamination of environmental samples was indicated, environmental samples associated with suspected contamination were not used in this analysis.

NAWQA sampling did not cover all areas of the United States. Some local, State, and Federal agencies have collected data on VOCs in aquifer studies with the same design characteristics and data-collection objectives as the NAWQA aquifer studies. The NAWQA Program has compiled some of these retrospective data sets. These retrospective data are considered to be similar enough in design to the NAWQA aquifer studies to augment them and provide a broader national coverage of ground-water quality.

Data on VOCs in ground water from more than 16,000 wells from about 50 ambient monitoring programs or other studies have been compiled as part of this retrospective effort. Retrospective data were used to supplement NAWQA data only if they met specific criteria in terms of monitoring objectives, design, well construction, methods of sample collection, laboratory analysis, and quality control (Lapham and Tadayon, 1996). Details of the design of the compilation effort and the sampling and analytical criteria required for selection of retrospective data can be found in Lapham and Tadayon (1996).

Retrospective data from 1,185 wells have been included in this report to supplement the NAWQA aquifer study data. The number of samples of ground water available from retrospective data for each solvent was as follows: methylene chloride, 1,177; PCE, 1,185; TCA, 1,185; and TCE, 1,185. Adding in the data from wells sampled by NAWQA, the total number of samples of ground water analyzed for each solvent was as follows: methylene chloride, 5,054; PCE, 4,996; TCA, 5,068; and TCE, 5,064.

Like NAWQA data, no samples were collected from nested wells in the retrospective data, and thus, each well represents a distinct geographic site. Only one sample of ground water from each well in the retrospective data was included in this report, and thus, the term sample is synonymous with well. If more than one sample from a well was available, the most recent sample was selected. Because of variations in design and data-collection objectives, all of the four solvents were not analyzed in all ground-water samples in the retrospective data set. The numbers of samples in the retrospective data that have concentration results for each solvent, by well type, are given in table 5.

For retrospective data, careful selection procedures were used to ensure their quality for inclusion in a national assessment. Only VOC analyses performed by GC/MS in a laboratory certified by the USEPA were included. Details of the requirements of the retrospective data for inclusion in the assessment have been published elsewhere (Lapham and Tadayon, 1996; Lapham and others, 2000).

Table 5. Number of ground-water samples with concentration results for solvents by well type for retrospective data.

[PCE, perchloroethene; TCA, 1,1,1-trichloroethane; TCE, trichloroethene]

Well type	Methylene chloride	PCE	TCA	TCE
Public	192	192	192	192
Domestic	515	517	517	517
Monitoring	194	199	199	199
Other	276	277	277	277
Total	1,177	1,185	1,185	1,185

Retrospective data compiled by NAWQA were analyzed for as many as 55 of the VOCs included in NAWQA's national assessment (Bender and others, 1999). However, in many cases samples were analyzed for a smaller subset of VOCs. For inclusion into the data used in this report, samples from retrospective data were required to be analyzed for at least 17 VOCs.

Source-Water Data

Data from another study were used to determine the occurrence, distribution, and status of solvents in ground water used as a source of drinking water for CWSs. This national source-water 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 main purpose of this survey was to determine the occurrence and distribution of the gasoline oxygenate methyl *tert*-butyl ether (MTBE) in both ground and surface water that served as source water for CWSs. However, samples were analyzed for a suite of VOCs to determine their occurrence in source water for CWSs.

Two phases of the source-water survey, with respect to ground water, were accomplished: (1) a random survey of 579 CWSs with ground-water sources throughout the country, and (2) a focused survey of 79 CWSs with ground-water solvent sources throughout the country that were considered susceptible to MTBE contamination (Clawges and others, 2001). In this analysis, only data from the random survey were included in order to avoid potential bias in the distribution of solvent sources. The selection of CWSs sampled in the random survey was statistically based and random and was stratified by population-served size category and total number of people served (Ivahnenko and others, 2001). More details on the design of the random survey were presented by Ivahnenko and others (2001). Results of the random survey were presented by Grady (2003).

Detailed explanations of the field and laboratory methods used in the source-water survey are described in Koch and others (2003). Samples of source water were analyzed for VOCs at the MWDSC laboratory in LaVerne, California. VOC analyses were performed using USEPA approved method 524.2 (Ivahnenko and others, 2001). Each sample from these wells was analyzed for 66 VOCs including each of the four solvents examined in this report.

All source-water wells were public-supply wells. Samples were collected at the wellhead, or as close to the wellhead as possible and before any treatment or blending. No samples were collected from nested wells in the source-water data, and thus, each well represents a distinct geographic site. Like NAWQA and retrospective data, only one sample of ground water from each well in the source-water data was included in this report, and thus, the term sample is synonymous with well. If more than one sample from a well was available, the most recent

sample was selected. The number of samples of source water available for each solvent was as follows: methylene chloride, 577; PCE, 577; TCA, 578; and TCE, 577.

Drinking-Water Data

Data on solvents in drinking water were compiled by the USGS from State drinking-water agencies in 12 Northeast and Mid-Atlantic States. The purpose of this survey was to describe the occurrence and distribution of MTBE and other VOCs in public drinking water supplied by CWSs in these two regions. These two regions were selected because they are generally highly populated, have a long-term history of urbanization, and are areas with high use of public-water supply (Grady and Casey, 2001; Moran and others, 2001). A random subset of all CWSs in the two regions was selected using a statistical approach that stratified selection by State, source of water, and number of people served by the utility (Grady and Casey, 2001).

The drinking-water data represented CWSs with water supplied exclusively by surface water, supplied exclusively by ground water, or supplied by a combination of surface and ground water. In this report, only data from CWSs supplied exclusively by ground water were included. Data on solvents were available for a total of 1,682 CWSs supplied exclusively by ground water.

The drinking-water data represent samples collected to meet the monitoring requirements of the Safe Drinking Water Act (SDWA). The samples were collected from 1993–1998 and were analyzed by a variety of State and private laboratories. Most analyses for SDWA compliance use USEPA methods 502.2 or 524.2 for determining VOC occurrence (Grady and Casey, 2001). In most cases, analyses for 21 regulated and 21 unregulated VOCs are determined routinely in drinking-water samples analyzed for SDWA compliance (Grady and Casey, 2001). Because the four solvents have MCLs, they are monitored in public drinking water regulated under the SDWA.

Multiple samples of drinking water from each CWS were available for the analysis period of 1993–1998. In this analysis, the occurrence of solvents was reported by CWS and not by sample because the number of samples available by CWS was highly variable. This variability can significantly skew the detection frequencies. Therefore, the data on drinking water were summarized by system. A CWS was counted as having a detection of a solvent if a measurable concentration of a solvent was reported in any one or more water samples for that CWS. However, concentration information on solvents in drinking water, such as median concentration, generally was computed using all samples available for each CWS. Using all detected concentrations avoided bias in selection of specific concentrations by CWS.

Solvent data were available for a total of 1,682 CWSs. The number of systems with data on each individual solvent in drinking-water samples was as follows: methylene chloride, 1,680; PCE, 1,681; TCA, 1,678; and TCE, 1,681.

Computational Procedures

The detection frequency of solvents in ground water was computed in several ways. For each solvent in ground water, and for one or more solvents in ground water, uncensored detection frequencies were computed as the number of wells with a detection of the solvent, or one or more solvents, divided by the number of wells in which the solvent, or one or more solvents, was analyzed. Although the laboratory reporting levels of the individual solvents were variable, these uncensored detection frequencies represent the best estimate of the overall occurrence of each solvent in ground water.

It has been shown that the detection frequency computed for a VOC is strongly dependent on the laboratory reporting level for the analyte (Lapham and others, 2000). Comparisons of detection frequencies between water-quality analytes that have different laboratory reporting levels may not reflect true differences in water quality. Instead, differences in detection frequencies between water-quality analytes may simply represent differences in instrument performance, instrument sensitivity, equipment operators, or laboratory conditions.

The laboratory reporting level is the minimum concentration value at which a laboratory will report the concentration of an analyte in water within a specified level of confidence. Although the laboratory reporting levels of individual solvents were variable, a good measure of the overall analytical resolution of each solvent is the median reporting level. Table 6 shows the median laboratory reporting level for each solvent in ground water as well as in source water and drinking water. The range in reporting levels for each solvent for each source of data also is shown in table 6.

For ground water, the median laboratory reporting levels of each solvent were the same. However, the range of laboratory reporting levels varied for each compound (table 6). This variability was probably due to differences in instrument performance (which often is compound dependent), instrument sensitivity, equipment operators, and laboratory conditions.

For source water, the median laboratory reporting levels of each solvent were different from one another. Also, the range of laboratory reporting levels varied within each compound

(table 6). Like ground-water data, this variability was probably due to differences in instrument performance, instrument sensitivity, equipment operators, and laboratory conditions.

For drinking water, the median laboratory reporting levels of each solvent were the same. However, like ground- and source-water data, the range of laboratory reporting levels varied within each compound (table 6). In this case, the variability was probably due, in part, to factors such as differences in the laboratory procedures and reporting levels for the various State and private laboratories that performed the analyses. Although the laboratory reporting levels for solvents in ground water, source water, and drinking water differed and were quite variable, it was possible to identify and isolate several uniform reporting levels common to all three data sets.

When comparing among solvents or among data sources, detection frequencies and concentrations were computed using a uniform assessment level. An assessment level is a fixed concentration for comparing water-quality results for analytes that have variable laboratory reporting levels. By equalizing the concentration at which detection frequencies and concentrations are compared, differences between individual solvents and different data sets can be determined.

For comparisons of solvent detection frequencies between individual solvents in data from ground water and source water, an assessment level of 0.2 µg/L was used. The median laboratory reporting levels for all four solvents in ground water were 0.2 µg/L (table 6). Although the median laboratory reporting levels for solvents in source water were less than 0.2 µg/L, all detected concentrations of VOCs in source water were assigned a minimum reporting level of 0.2 µg/L. This minimum reporting level was necessary because contamination of field quality-control samples in the source water data was common at concentrations less than 0.2 µg/L (David Bender, U.S. Geological Survey, written commun., 2005). Detected concentrations less than 0.2 µg/L in source water had low confidence of representing true environmental information. Thus, solvent data for source water had an effective laboratory censoring level of 0.2 µg/L.

Table 6. Median and range of laboratory reporting levels for solvents for each data source.

[µg/L, micrograms per liter; PCE, perchloroethene; TCA, 1,1,1-trichloroethane; TCE, trichloroethene]

Compound name	Median laboratory reporting level (µg/L)			Range in laboratory reporting levels (µg/L)		
	Ground water	Source water	Drinking water	Ground water	Source water	Drinking water
Methylene chloride	0.2	0.042	0.5	0.02–16	0.03–0.18	0.031–3
PCE	.2	.098	.5	0.02–0.5	0.05–0.19	0.037–4
TCA	.2	.09	.5	0.02–0.5	0.05–0.19	0.044–3
TCE	.2	.068	.5	0.02–0.5	0.04–0.19	0.03–3

The median laboratory reporting levels for all four solvents in drinking water were 0.5 µg/L (table 6). Although this is higher than 0.2 µg/L, the range in the reporting levels of drinking water extended below 0.2 µg/L (table 6). Additionally, the detection frequencies of solvents in drinking water were not different between assessment levels of 0.5 µg/L and 0.2 µg/L. Therefore, for consistency with ground water and source water, an assessment level of 0.2 µg/L was used for comparisons of detection frequencies between individual solvents in drinking water.

For comparisons of detection frequencies of solvents among all three data sources, an assessment level of 0.2 µg/L was used. This assessment level was selected because detection frequencies of individual solvents in all three data sources were computed at this concentration, and the detection frequencies were assumed to be accurate at this concentration. Using an assessment level of 0.2 µg/L, rather than a lower assessment level, also allowed for results obtained in this report to be compared to data from other work with higher reporting levels.

One additional assessment level for ground water was identified. Prior to April 1996, the laboratory reporting level used by the NWQL for most VOCs was 0.2 µg/L. Implementation of a new low-level analytical method after this date resulted in lower laboratory reporting levels for many compounds (Oblinger Childress and others, 1999). However, many compounds have laboratory reporting levels that vary as method changes are implemented or new instrumentation is used (Oblinger Childress and others, 1999).

Table 7 presents the median and range in laboratory reporting levels for the solvents in ground water analyzed by the NWQL using the new low-level method. For the low-level method, the laboratory reporting level is defined as a level that confines the rate of false positives and false negatives to less than 1 percent (Oblinger Childress and others, 1999). Unlike the composite ground-water data, the median and ranges in laboratory reporting levels for the solvents in this data subset are lower and more variable (table 7). The higher median laboratory reporting level for methylene chloride compared to the other solvents (table 7) is a result of methylene chloride being a frequent laboratory contaminant during much of the analysis period. This required a higher reporting level for methylene chloride. In addition, the new low-level reporting conventions used by the NWQL allowed for quantification of VOC concentrations below the laboratory reporting levels. A review of the reporting conventions for the new low-level method can be found in Moran and others (in press).

The minimum laboratory reporting level for all four solvents analyzed with the new low-level method was near 0.02 µg/L, and a large percentage of detected concentrations for each solvent were greater than or equal to 0.02 µg/L (table 7). Thus, an additional assessment level of 0.02 µg/L was applied to solvent concentrations determined using the new low-level method. This assessment level for low-level analyses is consistent with methods used in a national assessment of VOCs in the

Nation's aquifers by NAWQA (Moran and others, in press). The low-level analyses only were performed for a subset of all NAWQA-sampled wells analyzed after April 1996. The number of samples that had the low-level analyses for one or more solvents was 2,333. The number of samples that had low-level analyses for each individual solvent was as follows: methylene chloride, 2,331; PCE, 2,297; TCA, 2,333; TCE, 2,332.

To accurately compute detection frequency at a specific assessment level, non-detect values above the assessment level should be removed from the data set (Lapham and others, 2000). However, this can cause a substantial loss of data. For the analyses performed here, an unacceptable loss of data would occur using this method; therefore, a simplified approach to computing detection frequencies was used. Non-detect values above the assessment level were not removed from the analysis and were considered to be the same as non-detects below the assessment level. Using this approach did not result in detection frequencies significantly different from the approach where non-detects are removed. A detailed review of the assessment level concept and its application can be found in Lapham and others (2000).

Comparisons of detected concentrations between solvents and other VOCs also were made using an assessment level. This was done to ensure that comparisons were equitable between VOCs with variable laboratory reporting levels. For NAWQA data, comparisons of concentrations were made only with the low-level analyses, and with an assessment level of 0.02 µg/L. The low-level data were used because they were believed to more fully represent the range in environmental concentrations. For data on source water and drinking water, comparisons of concentrations between solvents and other VOCs were made at an assessment level of 0.2 µg/L. For comparisons of concentrations among all three data sets, an assessment level of 0.2 µg/L was used.

Table 7. Median and range of laboratory reporting levels for solvents analyzed using the National Water Quality Laboratory's low-level method.

[µg/L, micrograms per liter; ≥, greater than or equal to; PCE, perchloroethene; TCA, 1,1,1-trichoroethane; TCE, trichoroethene]

Compound name	Median laboratory reporting level (µg/L)	Range in laboratory reporting levels (µg/L)	Percent of quantified concentrations ≥0.02 µg/L
Methylene chloride	0.38	0.06–7.57	73
PCE	.1	0.027–0.5	61
TCA	.032	0.032–0.5	57
TCE	.038	0.038–0.5	71

Mixtures of solvents also were computed using an assessment level. The detection frequencies of mixtures of solvents were determined by dividing the number of times that two or more unique combinations of solvents were detected in a sample by the number of times all solvents in the mixture were analyzed together, at a specific assessment level. The total number of unique combinations of two or more solvents detected in a sample is given by the equation (Sheskin, 1997):

$$\sum_{x=2}^{i} \frac{i!}{x!(i-x)!}$$

where

    x = number of VOCs in mixture, and

    i = number of detected VOCs.

For ground water, assessment levels of 0.2 µg/L and 0.02 µg/L were used in computing mixture detection frequencies and mixture median concentrations. For source water, an assessment level of 0.2 µg/L was used in computing mixture detection frequencies and mixture median concentrations. Because data on solvents in drinking water were summarized by CWS, an analysis of mixtures would not be meaningful and was not attempted.

An important point to note is that quantified concentrations of solvents less than 0.02 µg/L exist in the ground-water data set, although they generally were not considered when computing detection frequencies or examining concentrations at either assessment level. The presence of low concentration information on VOCs was a result of the unique, information-rich nature of the analytical method used by the NWQL. Details of the information-rich methodology used by the NWQL can be found in Connor and others (1998) and Oblinger Childress and others (1999).

When examining detection frequencies, concentrations, or frequencies of concentrations exceeding the MCL, the four solvents often were compared to the 55 VOCs that were included in NAWQA's national assessment of VOCs (Bender and others, 1999). These VOCs were chosen through a rigorous identification and selection process and represent compounds that have important physical, chemical, and biological properties. Most of these VOCs also have enforceable drinking-water standards or other important human-health effects (Bender and others, 1999). Only 24 of the 55 examined VOCs have MCLs. The VOCs with MCLs and their MCL values are given in Appendix 1. The MCL for trihalomethanes (THMs) applies to the sum of all four THM compounds in a sample—chloroform, bromoform, bromodichloromethane, and dibromochloromethane. The MCL for xylenes applies to the sum of all three xylenes isomers in a sample—*o*-xylene, *m*-xylene, and *p*-xylene.

Comparisons of solvents to the 55 VOCs were limited to the ranking of each VOC with respect to detection frequencies, concentrations, or frequencies of concentrations exceeding the MCL. The ranking of each VOC for each of these statistics in each data source is given in Appendixes 2–10. For ground

water, most samples were analyzed for all of the 55 VOCs. Samples in the retrospective data sometimes were analyzed for fewer than the 55 VOCs, but each sample was required to be analyzed for a minimum of 17 of these compounds to be included in this report. For source water, samples were analyzed for only 52 of the 55 VOCs. For drinking water, samples were analyzed for only 51 of the 55 VOCs.

Statistical Tests

A variety of statistical tests were performed to analyze the data on solvents in ground water, source water, and drinking water to better understand their meaning. In all cases, nonparametric statistical tests were used because the data were not assumed to have any particular distribution. For all tests in this report, a level of statistical significance (α) of 0.05 was used, which is equivalent to a 95-percent confidence interval. Detailed information on the statistical tests used in this report can be found in Helsel and Hirsch (1992).

In the case of two or more categorical variables, a Pearson's chi-square test of independence, with Yates' continuity correction, was performed. Yates continuity correction was used to give a more conservative test of significance. In the case of two independent groups of continuous data, a Wilcoxon rank-sum test, or Mann-Whitney test, was performed. In the case of matched pairs of continuous data, a Wilcoxon signed-rank test was used. To determine a relation between two continuous variables, a Spearman correlation test was performed. For sample sizes <20, Kendall's tau test was performed to measure the strength of a monotonic relation between two variables.

For determining differences in the distributions of concentrations of solvents, quantile plots were used. Values less than the laboratory reporting level were given a default concentration value for plotting of 10^{-4}. Quantile plots allow for the comparison of the distribution of all concentrations of two or more solvents. To test the statistical significance of distributional differences, the nonparametric Kolmogorov-Smirnov test was used.

For determining associations between multiple explanatory variables and the probability of occurrence of solvents in ground water, multivariate logistic regression analyses were used. The regression results only were used to determine associations between solvent 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 the occurrence of solvents.

In logistic regression, the response or dependent variable is the occurrence, or non-occurrence, of one or more solvents or individual solvents. In its simplest form, the response variable is binary coded as 0 or 1, with 0 indicating a non-occurrence and 1 indicating an occurrence. The explanatory variables are then related to the probability of occurrence of the response variable

in a manner similar to linear regression. The magnitude and sign of the estimated slope coefficients determine the strength and direction of the association of explanatory variables with the probability of detecting solvents in water according to the following equation:

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

where

P = probability of detecting a solvent;

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 a solvent with an increase in the explanatory variable, whereas estimated coefficients with negative signs indicate a decrease in the probability of detecting a solvent with an increase in the explanatory variable. Uncorrected estimated slope coefficients do not give an accurate assessment of the strength of an association 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 directly between one another. 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). Standardized coefficients were computed following 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 occurrence of a solvent. 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 of the coefficient was used to determine significance. 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 occurrence of a solvent.

An additional test was performed to evaluate the logistic regression analyses. The Hosmer-Lemeshow test was used to assess how well the observed binary responses were predicted by the model equation (Hosmer and Lemeshow, 1989). The null hypothesis for this test is that the predicted responses are identical to the observed responses. Therefore, a higher p-value for this test indicates a better correspondence between the observed and predicted responses.

A variety of explanatory data were used in the logistic regression analyses. These data represented various hydrogeo-logic and anthropogenic factors that could control or influence the sources, transport, or fate of solvents in ground water. Table 8 lists the hydrogeologic and anthropogenic variables that were used in the logistic regression analyses. Included in this table are the units for each variable, a description of each variable, the coding of each variable in the regression analyses, and the source of the data for each variable. In the logistic regression analyses, density, percent, polygon, and point data were averaged for a 500-m radius around each well. In some cases, density data also were estimated for each well as an average for a 1-kilometer (km) radius around each well.

Occurrence of Solvents

The occurrence of solvents was examined in seven main sections: (1) the occurrence and distribution of solvents in ground water, (2) the occurrence and distribution of solvents in source water, (3) the occurrence and distribution of solvents in drinking water, (4) the concentrations of solvents in ground water, (5) the concentrations of solvents in source water, (6) the concentrations of solvents in drinking water, and (7) comparisons of the occurrence and concentrations of solvents among all three data sets.

Occurrence and Distribution of Solvents in Ground Water

Without applying an assessment level, one or more of the four solvents were detected in 881 of 5,068 samples of ground water, or 17 percent. Without applying an assessment level, the detection frequencies of each solvent were as follows: PCE, 11 percent; TCA, 7 percent; TCE, 5 percent; and methylene chloride, 3 percent.

At assessment levels of 0.2 µg/L and 0.02 µg/L, the detection frequencies of one or more solvents in ground water were 7 percent and 18 percent, respectively. Relative to the 55 VOCs included in NAWQA's national assessment of VOCs, the ranking of detection frequencies of solvents in ground water were as follows: PCE, 3; TCE , 4; TCA, 5; and methylene chloride, 13 (Appendix 2). The assessment level used was 0.2 µg/L, and 43 of the 55 VOCs were detected in one or more samples at 0.2 µg/L. The detection frequencies of the solvents were higher than most other VOCs and were in the top 5 most frequently detected VOCs, with the exception of methylene chloride.

The detection frequencies of each solvent in ground water, at an assessment level of 0.2 µg/L, are shown in figure 3. At this assessment level, PCE had the highest detection frequency followed by TCE, TCA, and methylene chloride. The detection frequencies of each solvent in ground water at an assessment level of 0.02 µg/L also are shown in figure 3. For each individual solvent, the detection frequency of solvents in ground water was higher at an assessment level of 0.02 µg/L than at an assessment level of 0.2 µg/L. At an assessment level of 0.02 µg/L, the detection frequency of PCE was highest, followed by TCA, TCE, and methylene chloride.

Table 8. Hydrogeologic and anthropogenic variables that were used in the logistic regression analyses of solvents in ground water.

[mm/yr, millimeters per year; in/hr, inches per hour; g/cm^3, grams per cubic centimeter; ft, feet; in., inch; °C, degrees Celsius; µS/cm, microsiemens per centimeter; km, kilometer; km^2, square kilometer; yr, year; 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, Toxic Release Inventory; CERCLA, Comprehensive Environmental Response, Compensation, and Liability Act; RCRA, Resource Conservation and Recovery Act; S, source; T, transport; F, fate]

Variable (type)	Units	Description	Coding	Source
Hydrogeologic variables				
Recharge (T)	mm/yr	average recharge	continuous	Wolock (2003)
Soil permeability (T)	in/hr	average soil permeability by soil unit	continuous	Wolock (1997)
Soil sand (T)	percent	average soil sand content by soil unit	0–100	Wolock (1997)
Soil silt (T)	percent	average soil silt content by soil unit	0–100	Wolock (1997)
Soil clay (T)	percent	average soil clay content by soil unit	0–100	Wolock (1997)
Soil organic matter (T)	percent	average organic matter content by soil unit	0–100	Wolock (1997)
Soil bulk density (T)	g/cm^3	average bulk density of soil by soil unit	continuous	Wolock (1997)
Soil erodibility (T)	unitless	soil erosion rate per soil erosion unit	0.02–0.69	Wolock (1997)
Vertical soil permeability (T)	in/hr	average vertical soil permeability by soil unit	continuous	Wolock (1997)
Hydric soils (T)	percent	average percent hydric soils by soil unit	0–100	Wolock (1997)
Available water capacity (T)	fraction	average water fraction by soil unit	0–1	Wolock (1997)
Slope of land surface (T)	percent	average slope of land surface by soil unit	0–100	Wolock (1997)
Seasonal water level (T)	ft	average depth to seasonally high water table by soil unit	continuous	Wolock (1997)
Soil thickness (T)	in.	average depth to bedrock by soil unit	continuous	Wolock (1997)
Precipitation (T)	cm	average estimated annual precipitation	continuous	U.S. Department of Commerce (1995)
Temperature (T)	°C	average estimated annual temperature	continuous	U.S. Department of Commerce (1995)
Well casing diameter (T)	ft	average casing diameter by well	continuous	GWSI
Well depth (T)	ft	total depth of well	continuous	GWSI
Water level (T)	ft	average water level by well		GWSI
Depth to top of screened interval (T)	ft	depth to the top of the screened interval in the well	continuous	GWSI
Aquifer confinement (T)	unitless	confining condition of the aquifer	1 - unconfined; 0.5 - mixed; 0 - confined	GWSI
Temperature of ground water (F)	°C	average temperature of water in the well	continuous	GWSI
Dissolved oxygen (F)	mg/L	average dissolved oxygen content of water in the well	continuous	QWDATA
Specific conductance (F)	µS/cm	average specific conductance of water in the well	continuous	QWDATA

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

Variable (type)	Units	Description	Coding	Source
Anthropogenic variables				
Population (S)	persons/km^2	block group population	continuous	Bureau of the Census (1991); CIESIN (1995); Dobson and others (2000)
Septic system sewerage (S)	percent	block group percent of households	0–100	Bureau of the Census (1991)
Public sewerage (S)	percent	block group percent of households	0–100	Bureau of the Census (1991)
Other sewerage (S)	percent	block group percent of households	0–100	Bureau of the Census (1991)
Public water supply usage (S)	percent	block group percent of households	0–100	Bureau of the Census (1991)
Domestic water supply usage (S)	percent	block group percent of households	0–100	Bureau of the Census (1991)
Households with drilled wells (S)	percent	block group percent of households	0–100	Bureau of the Census (1991)
Households with dug wells (S)	percent	block group percent of households	0–100	Bureau of the Census (1991)
Households with other water service (S)	percent	block group percent of households	0–100	Bureau of the Census (1991)
Year of home construction (S)	yr	block group median age of home construction	0–100	Bureau of the Census (1991)
Leaking gasoline underground storage tanks (S)	count	number of sites within 1 km of well	continuous	Vista Information Solutions (1999)
Leaking dry-cleaning underground storage tanks (S)	count	number of sites within 1 km of well	continuous	Vista Information Solutions (1999)
Gasoline underground storage tanks (S)	count	number of sites within 1 km of well	continuous	Vista Information Solutions (1999)
Dry-cleaning underground storage tanks (S)	count	number of sites within 1 km of well	continuous	Vista Information Solutions (1999)
Septic systems	count	number of sites within 1 km of well	continuous	Bureau of the Census (1991)
Urban land use (S)	percent	average land use around well	0–100	USGS (1999); Wright and others (1995); Vogelmann and others (2001); C.V. Price, USGS, written commun. (2004)
Agricultural land use (S)	percent	average land use around well	0–100	USGS (1999); Wright and others (1995); Vogelmann and others (2001); C.V. Price, USGS, written commun. (2004)
Undeveloped land use (S)	percent	average land use around well	0–100	USGS (1999); Wright and others (1995); Vogelmann and others (2001); C.V. Price, USGS, written commun. (2004)
Roads (S)	percent	average percent road area around well	0–100	Bureau of the Census (1991)
TRI sites (S)	count	number of sites within 1 km of well	continuous	USEPA (2004b)
CERCLA sites (S)	count	number of sites within 1 km of well	continuous	USEPA (2004b)
RCRA sites (S)	count	number of sites within 1 km of well	continuous	USEPA (2004b)
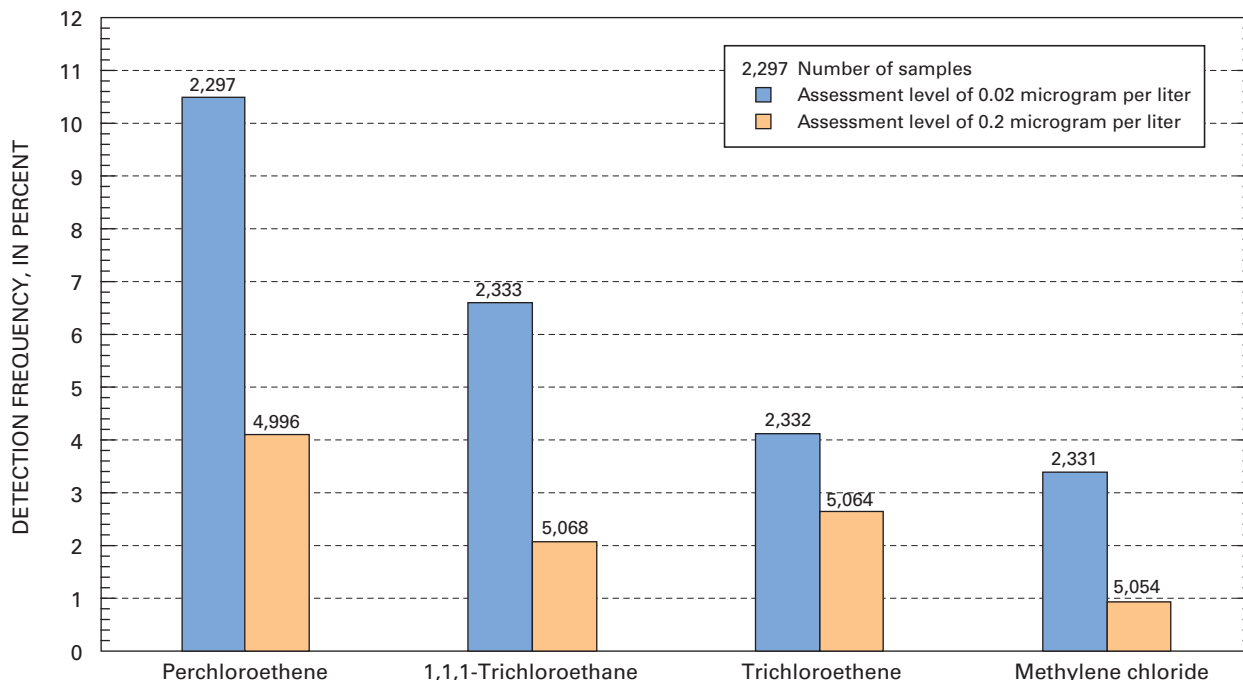
Figure 3. Detection frequencies of four solvents in ground water.

The detection frequencies of individual solvents by NAWQA study type and at an assessment level of 0.2 µg/L are illustrated in figure 4. At an assessment level of 0.2 µg/L, one or more solvents were detected in samples from 218 of 3,498 wells (6 percent) in aquifer studies, 120 of 847 wells (14 percent) in shallow ground-water studies in urban areas, and 12 of 723 wells (2 percent) in shallow ground-water studies in agricultural areas. The detection frequency of each solvent was higher in urban areas and lower in agricultural areas compared to aquifer studies (fig. 4).

The pattern of detection frequencies of solvents was similar in shallow ground-water studies in urban areas and aquifer studies with detection frequencies highest for PCE, followed by TCA, TCE, and methylene chloride (fig. 4). However, the pattern of solvent detections was different in shallow ground-water studies in agricultural areas with detection frequencies highest for methylene chloride followed by TCE, PCE, and TCA. The source of PCE in studies in urban areas and in aquifer studies probably is releases of the solvent from industrial and commercial facilities where it is used, like dry cleaners. The source of methylene chloride in agricultural areas could be the transformation of carbon tetrachloride, which was used as a fumigant in grain storage bins (U.S. Department of Agriculture, 2005).

At an assessment level of 0.02 µg/L, one or more solvents were detected in samples from 248 of 1,687 wells (15 percent) in aquifer studies, 159 of 548 wells (29 percent) in studies in urban areas, and 19 of 98 wells (19 percent) in studies in

agricultural areas. The detection frequency of each individual solvent, with the exception of methylene chloride, was higher in studies in urban areas than in aquifer studies (fig. 5). The detection frequencies of PCE and TCA were higher in studies in agricultural areas than in aquifer studies. The source of low concentrations of PCE and TCA in studies in agricultural areas is not clear but these compounds may be active or inert ingredients in pesticide formulations (Grady and Mullaney, 1998). Few samples from studies in agricultural areas were available for analyses of solvents at 0.02 µg/L. The samples were located in only a few areas including eastern Iowa, eastern Tennessee, the Puget Sound area of Washington, and parts of New Jersey.

The distribution of detection frequencies of each solvent by each individual NAWQA study at an assessment level of 0.02 µg/L is shown in figure 6. The detection frequencies were computed for each individual study and grouped into study types (urban areas, agricultural areas, and aquifer studies). The detection frequencies of individual solvents by individual study were highly variable. In most cases, the median detection frequency of solvents by individual study was higher in urban areas than in either agricultural areas or aquifer studies. The number of aquifer studies sampled was 57, and the number of shallow ground-water studies in urban areas sampled was 20. However, only four shallow ground-water studies in agricultural areas were analyzed for solvents using the low-level methods; therefore, the median detection frequencies for the agricultural areas, as shown in figure 6, are only estimates.
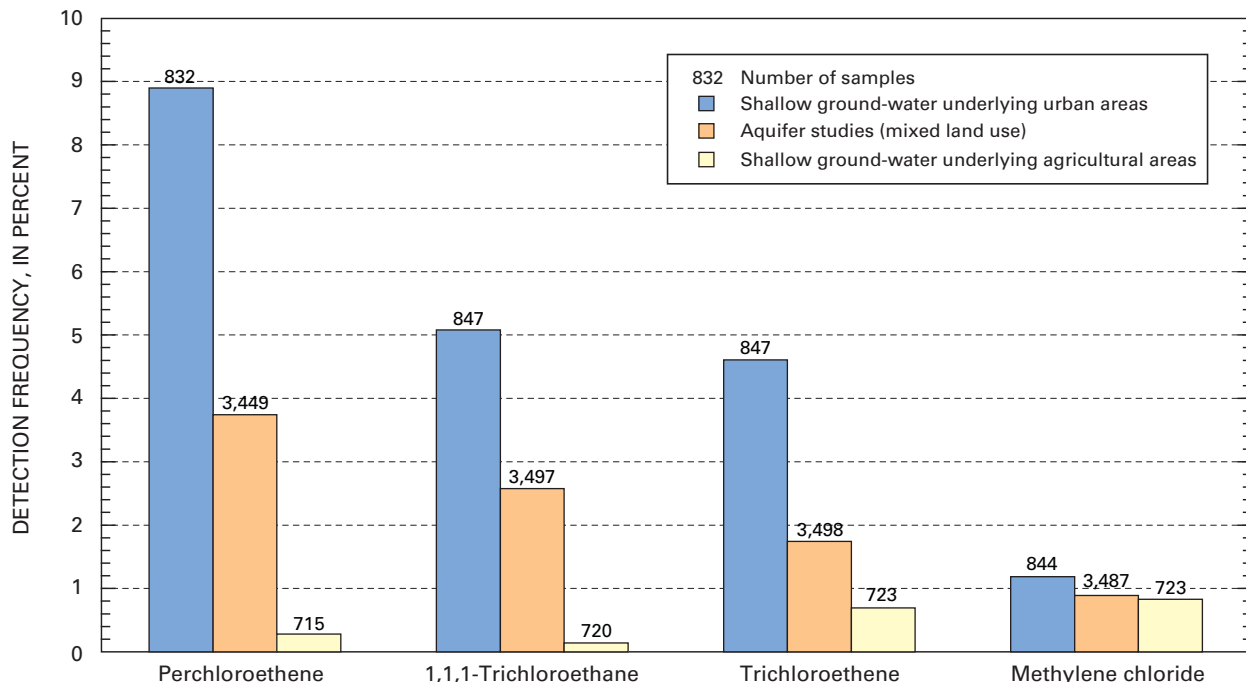
Figure 4. Detection frequencies of four solvents in ground water from National Water-Quality Assessment studies at an assessment level of 0.2 microgram per liter.
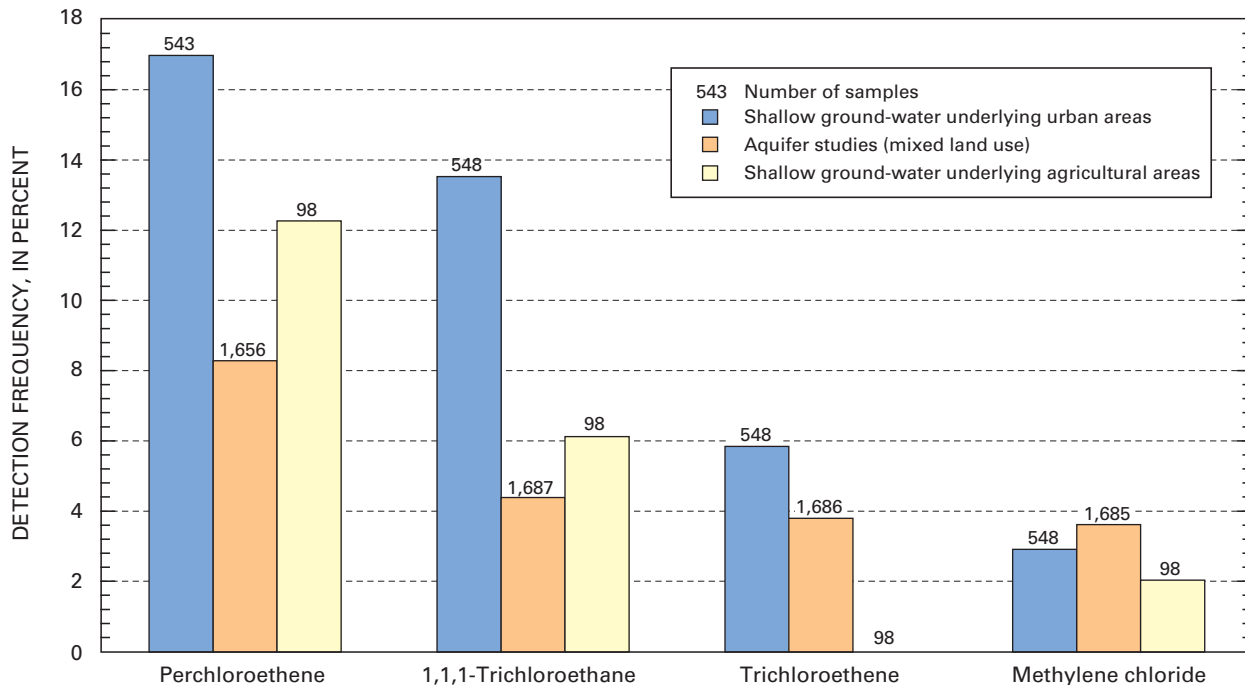
Figure 5. Detection frequencies of four solvents in ground water from National Water-Quality Assessment studies at an assessment level of 0.02 microgram per liter.
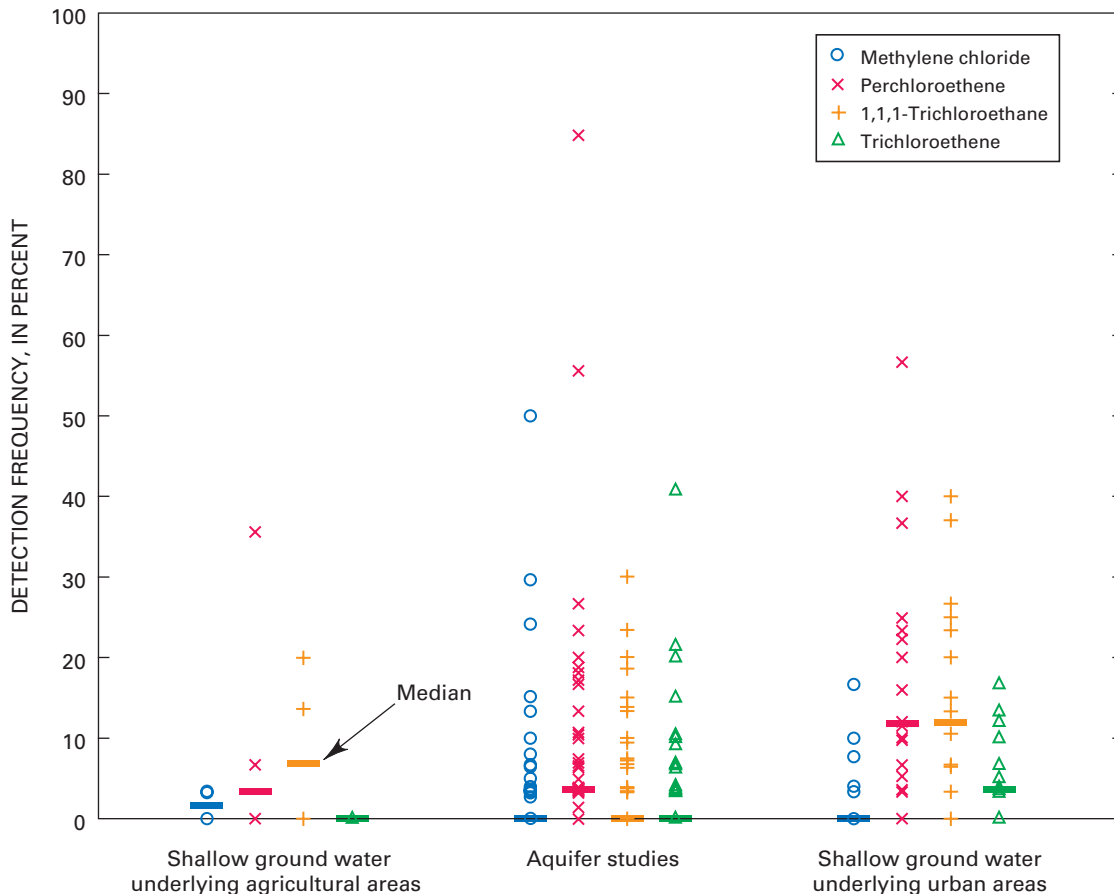
Figure 6.   Detection frequency of four solvents by individual study type at an assessment level of 0.02 microgram per liter.

The distribution of wells sampled for ground water for any of the four solvents and the distribution of wells where one or more solvents were detected is shown in figure 7. Without applying an assessment level, the detections of solvents were spread throughout the conterminous United States. Detections of solvents seemed to be concentrated in the Northeast region and several other locations such as eastern Iowa and California.

The distribution of wells sampled for each of the four solvents and the distribution of wells where each solvent was detected are shown in figures 8–11 for methylene chloride, PCE, TCA, and TCE, respectively. Without applying an assessment level, the detections of each solvent were spread throughout the conterminous United States. Detections of methylene chloride (fig. 8) appear to be concentrated in the Great Lakes area and eastern Iowa whereas detections of PCE (fig. 9) appear to be concentrated in the Northeast region and in eastern Iowa. Detections of TCA (fig. 10) and TCE (fig. 11) appear to be concentrated in the Northeast Region.

One or more of the four solvents examined in this report dominated mixtures of the 55 VOCs in ground water from aquifer studies. At an assessment level of 0.2 µg/L, 9 of the 10

most frequently occurring mixtures of VOCs in aquifer studies contained one or more of the four solvents (Zogorski and others, in press). The most frequently occurring mixture in aquifer studies was PCE-TCE, occurring in about 1.5 percent of samples (Zogorski and others, in press).

Mixtures were a common mode of occurrence among the four solvents in samples of ground water. At an assessment level of 0.2 µg/L, 30 percent of detections of any of the four solvents were mixtures of two or more solvents. At an assessment level of 0.02 µg/L, 27 percent of detections of any of the four solvents were mixtures of two or more solvents. However, when examined relative to the total number of samples of ground water, the detection frequency of mixtures was only 2 percent at an assessment level of 0.2 µg/L, and 5 percent at an assessment level of 0.02 µg/L.

Eleven unique mixtures of the four solvents are possible. The detection frequencies of each potential mixture in all ground-water samples are shown in table 9. Detection frequencies are given in table 9 at assessment levels of 0.2 and 0.02 µg/L for all samples and for a subset of samples with detections of one or more solvents.
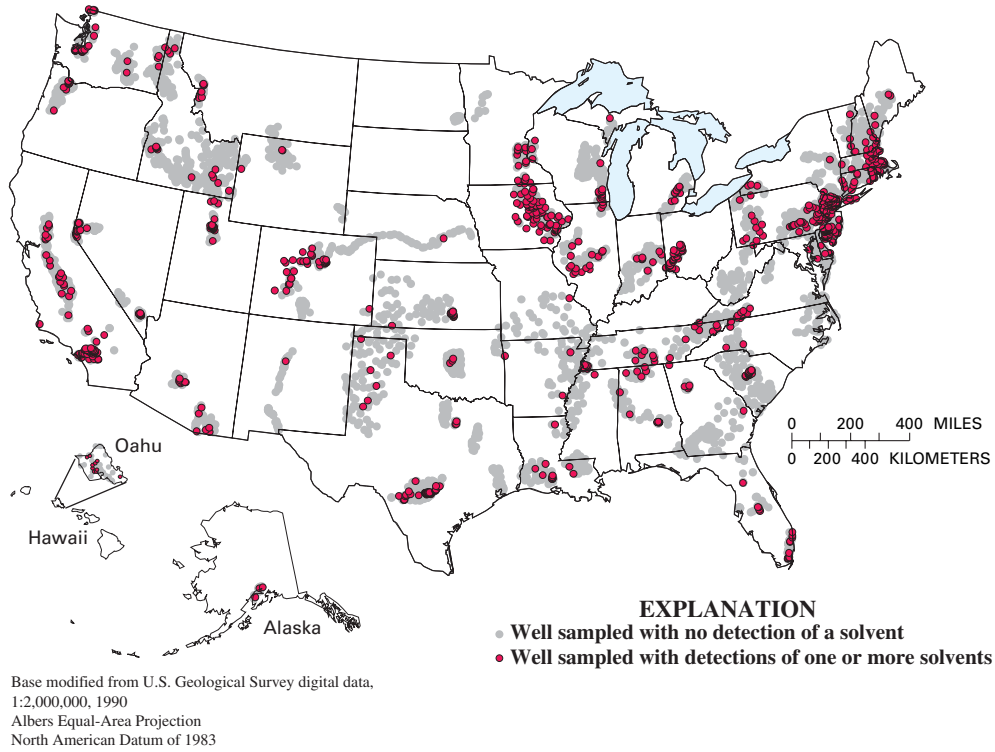
Figure 7. Locations where ground water was sampled for methylene chloride, perchloroethene, 1,1,1-tri-chloroethane, or trichloroethene and where one or more solvents were detected using no assessment level.
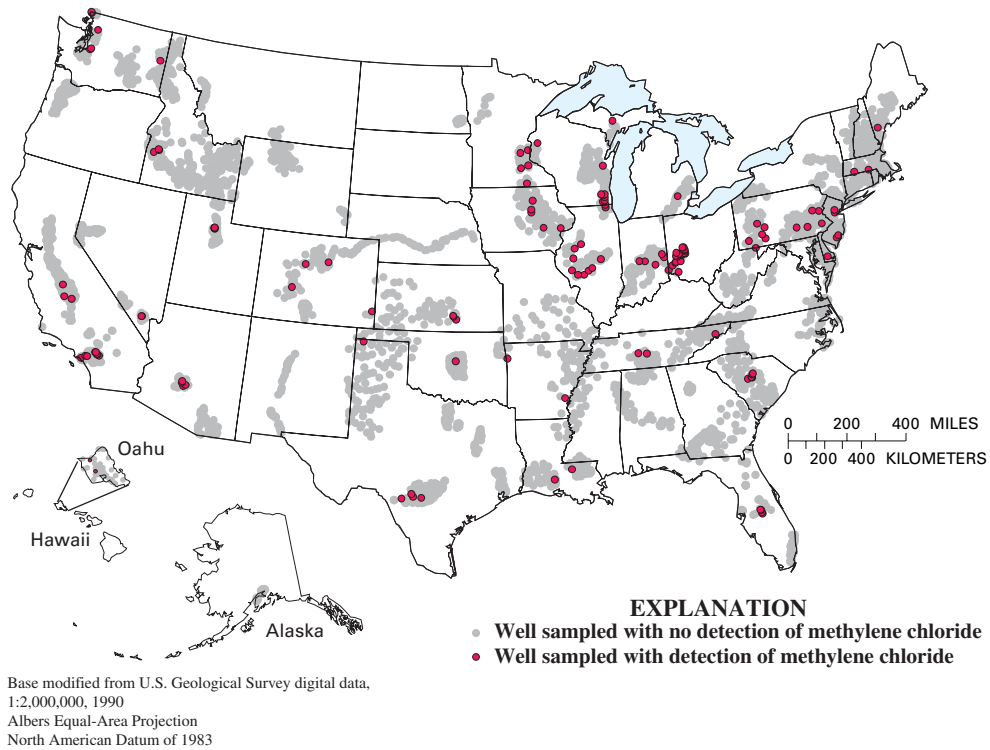
Figure 8. Locations where ground water was sampled for methylene chloride and where methylene chloride was detected using no assessment level.

Oahu

Hawaii

Alaska

EXPLANATION
- Well sampled with no detection of PCE
- Well sampled with detection of PCE

Base modified from U.S. Geological Survey digital data,
1:2,000,000, 1990
Albers Equal-Area Projection
North American Datum of 1983
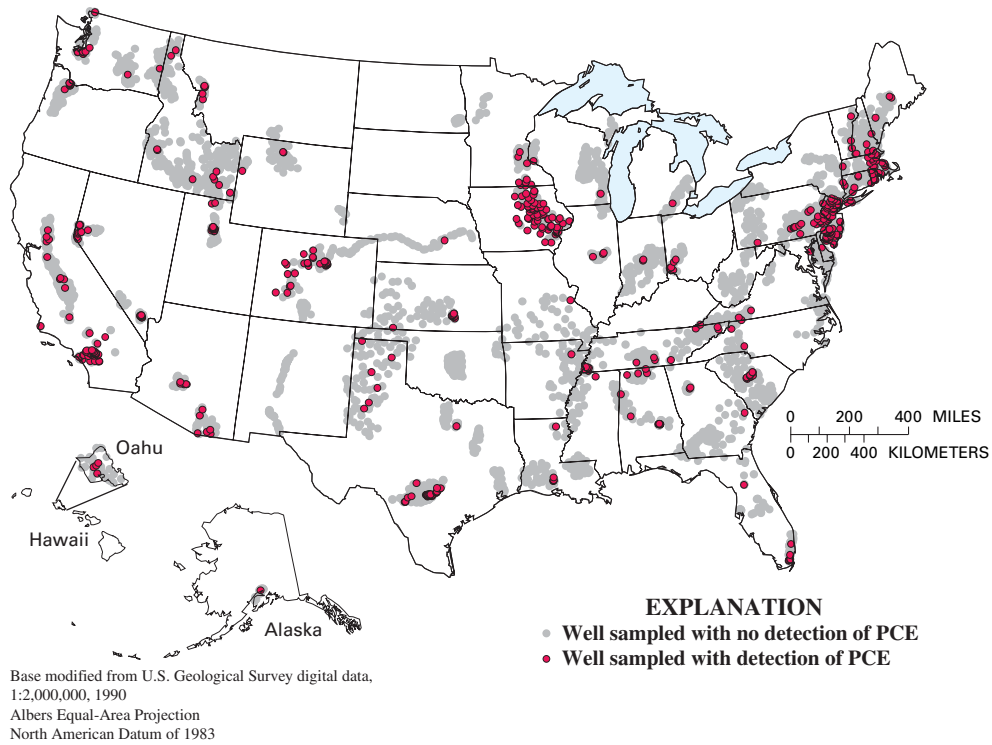
Figure 9.   Locations where ground water was sampled for perchloroethene (PCE) and where PCE was detected using no assessment level.

Oahu

Hawaii

Alaska

EXPLANATION
- Well sampled with no detection of TCA
- Well sampled with detection of TCA

Base modified from U.S. Geological Survey digital data,
1:2,000,000, 1990
Albers Equal-Area Projection
North American Datum of 1983
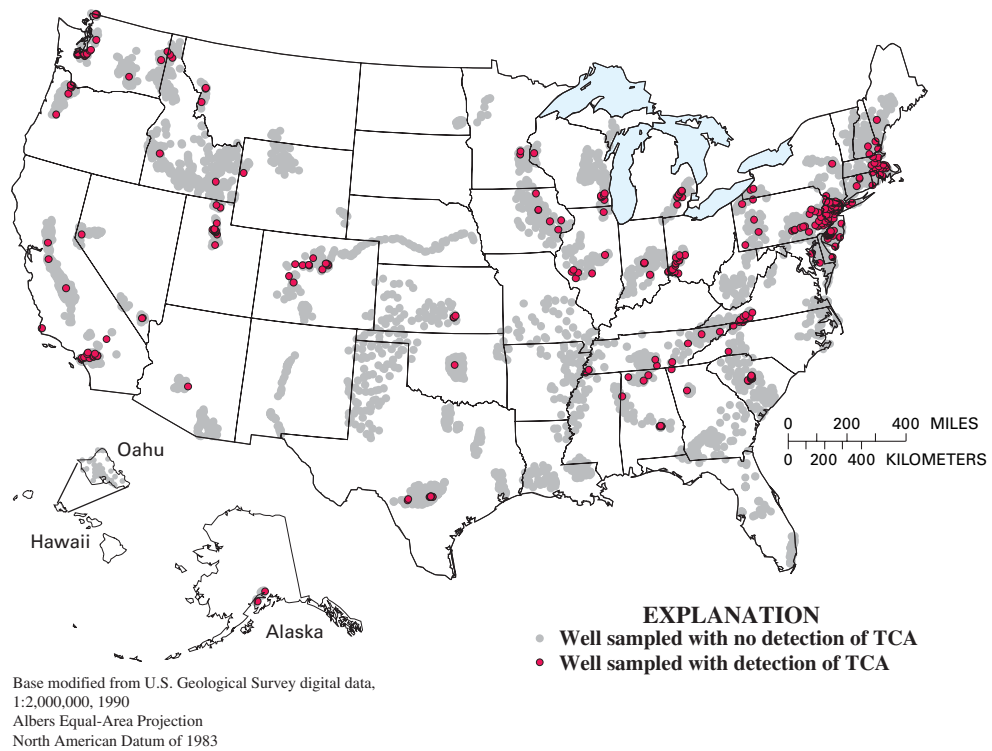
Figure 10.   Locations where ground water was sampled for 1,1,1-trichloroethane (TCA) and where TCA was detected using no assessment level.

Base modified from U.S. Geological Survey digital data,
1:2,000,000, 1990
Albers Equal-Area Projection
North American Datum of 1983
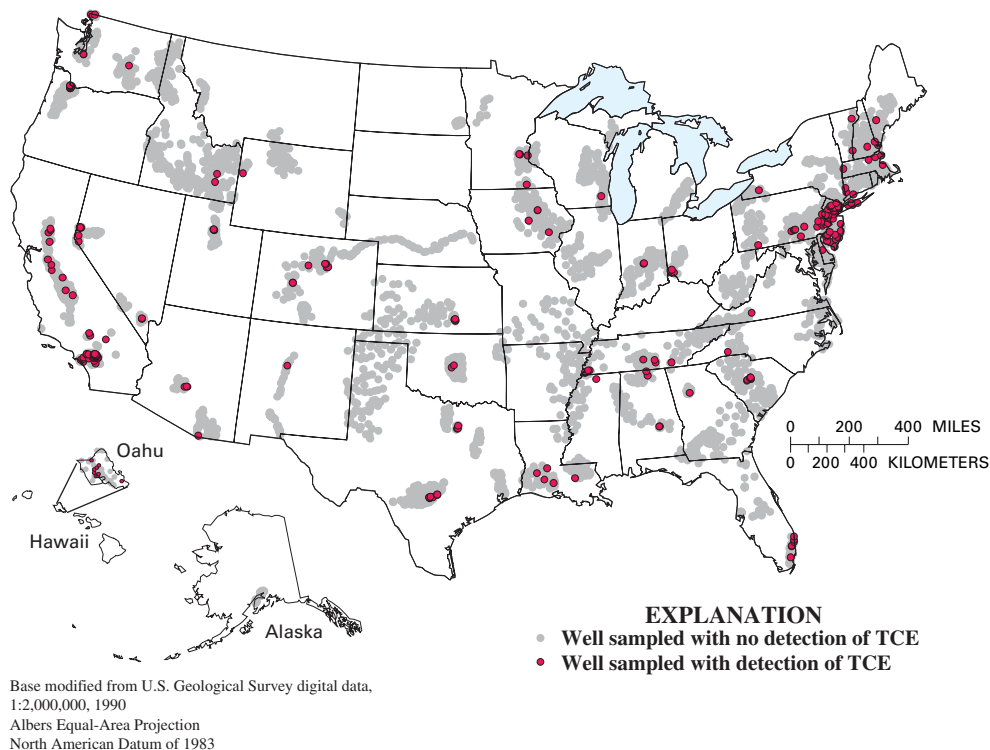
Figure 11.   Locations where ground water was sampled for trichloroethene (TCE) and where TCE was detected using no assessment level.

The combination of PCE and TCE was the most frequently occurring mixture at both assessment levels. At an assessment level of 0.02 µg/L, the mixture of PCE and TCA occurred as frequently as PCE and TCE. This may be due to the common usage of both PCE and TCA in metal degreasing and dry cleaning, and thus, common sources for both solvents (Halogenated Solvents Industry Alliance, 1994, 2005). In general, the most frequently occurring solvent mixtures were the same at assessment levels of 0.2 and 0.02 µg/L (table 9).

Occurrence and Distribution of Solvents in Source Water

At an assessment level of 0.2 µg/L, one or more solvents were detected in 36 of 579 samples of source water, or 6 percent. The detection frequencies of individual solvents were as follows: PCE, 4 percent; TCE, 3 percent; TCA, 2 percent; and methylene chloride, 0.2 percent (one sample).

The detection frequencies of the individual solvents in source water were higher than most other VOCs and were in the top 10 most frequently detected VOCs, with the exception of methylene chloride. Relative to 52 VOCs analyzed for in the source-water samples, the ranking of detection frequencies of solvents in source water was as follows: PCE, 6; TCE, 7; TCA,

10; and methylene chloride, 28 (Appendix 3). The assessment level used was 0.2 µg/L, and 40 of the 52 VOCs were detected in one or more samples.

The pattern of occurrence and detection frequencies of individual solvents in source water was very similar to that of ground water at an assessment level of 0.2 µg/L. This is expected as the quality of source water from ground water should be nearly the same as that of the ground-water resource itself.

Figure 12 shows the distribution of detections of one or more of the four solvents in source water throughout the United States. The detections of solvents in source water were distributed throughout the country. Because of the small number of detections for each individual solvent, their geographic distributions are not shown in this report.

Unlike ground water, solvents did not dominate mixtures involving VOCs in source water. Of the five most frequently occurring VOC mixtures in public well samples, of which the source-water survey was a major component, none contained one or more of the four solvents (Zogorski and others, in press). In public well samples, the most frequently occurring mixtures were various combinations of trihalomethanes (Zogorski and others, in press). This suggests different sources of VOCs to public wells than to ground water from aquifer studies.

Table 9. Detection frequencies and concentrations of 11 solvent mixtures in ground water nationwide at assessment levels of 0.2 microgram per liter and 0.02 microgram per liter.

[µg/L, micrograms per liter; PCE, perchloroethene; TCE, trichoroethene; TCA, 1,1,1-trichoroethane]

| Solvent mixture	Assessment level of 0.2 µg/L			Assessment level of 0.02 µg/L		
	Detection frequency in ground water (percent)		Median concentration of each solvent in mixture (µg/L)	Detection frequency in ground water (percent)		Median concentration of each solvent in mixture (µg/L)
	Denominator is all samples in which solvents were analyzed	Denominator is samples in which one or more solvents were detected		Denominator is all samples in which solvents were analyzed	Denominator is samples in which one or more solvents were detected	
PCE	1.5	21	2.0	2.6	14	0.17
TCE			1.0			0.14
PCE	0.9	13	1.1	2.6	14	0.07
TCA			0.4			0.07
TCE	0.8	11	1.5	1.3	7.0	0.14
TCA			0.8			0.06
PCE			2.3			0.15
TCE	0.5	7.7	2.0	1.1	5.9	0.15
TCA			0.8			0.06
PCE	0.2	2.6	0.7	0.6	3.3	0.16
Methylene chloride			1.7			0.09
TCE	0.2	2.3	1.3	0.2	1.2	0.15
Methylene chloride			1.8			0.06
TCA	0.1	1.7	0.7	0.3	1.9	0.13
Methylene chloride			0.6			0.04
PCE			0.9			0.32
TCE	0.1	2.0	1.4	0.2	1.2	0.15
Methylene chloride			1.9			0.06
PCE			2.4			0.39
TCA	0.1	1.1	0.8	0.1	0.7	0.08
Methylene chloride			25			0.05
TCE			1.1			1.13
TCA	0.1	1.4	0.8	0.1	0.7	0.08
Methylene chloride			0.7			0.05
PCE			2.4			0.39
TCE	0.1	1.1	4.3	0.1	0.7	1.13
TCA			0.8			0.08
Methylene chloride			25			0.05

Figure 12.   Locations where source water from ground water was sampled for methylene chloride, perchloroethene, 1,1,1-trichloroethane, or trichloroethene and where one or more solvents were detected at an assessment level of 0.2 microgram per liter.

Of the 36 samples of source water with one or more solvents, 15 contained two or more solvents. This is 42 percent of the samples with one or more solvents and about 3 percent of all samples of source water that were analyzed. The detection frequencies of each potential mixture in source water are shown in table 10. Only four mixtures of solvents were detected in source water at an assessment level of 0.2 µg/L. The mixture of PCE and TCE was most frequently occurring (table 10). No mixtures with methylene chloride occurred because this solvent only was detected once and not with any other solvent.

Occurrence and Distribution of Solvents in Drinking Water

At an assessment level of 0.2 µg/L, one or more of the four solvents were detected in samples of drinking water from 177 of 1,682 CWSs, or 11 percent, in 12 Northeast and Mid-Atlantic States. The detection frequencies of individual solvents were as follows: TCA, 5 percent; PCE, 4; percent; TCE, 4 percent; and methylene chloride, 3 percent. Because the drinking-water data consisted of multiple samples of solvents from each CWS, a CWS was counted as having a detection of a solvent if any sample in the CWS contained a detection of the solvent at the specified assessment level.

The detection frequencies of the individual solvents, with the exception of methylene chloride, in drinking water were higher than most other VOCs and were in the top 10 most frequently detected VOCs. Relative to 51 VOCs, the ranking of detection frequencies of solvents in drinking water was as follows: TCA, 6; PCE, 7; TCE, 8; and methylene chloride, 11 (Appendix 4). The assessment level used was 0.2 µg/L, and 44 of the 51 VOCs were detected in one or more samples at this assessment level.

Figure 13 shows the distribution of drinking water from CWSs sampled for solvents and the distribution of CWSs in which one or more solvents were detected. The data on solvents in drinking water from CWSs were only available for 12 Northeast and Mid-Atlantic States. The majority of solvent detections appeared to be in the more heavily populated areas of the regions along the coast.

The distribution of drinking water from CWSs where each of the four solvents was analyzed and the distribution of CWSs where each solvent was detected are shown in figures 14–17 for methylene chloride, PCE, TCA, and TCE, respectively. For the most part, no geographic pattern of occurrence was obvious in the distributions of detections of individual solvents. Because the occurrence of solvents in drinking water was reported by CWS and not by sample, no meaningful analysis of mixtures of solvents in drinking water could be performed.

Table 10. Detection frequencies of 11 solvent mixtures in source water nationwide at an assessment level of 0.2 microgram per liter.

[NA, not applicable; μg/L, microgram per liter; PCE, perchloroethene; TCE, trichoroethene; TCA, 1,1,1-trichoroethane]

Solvent mixture	Detection frequency in source water (percent)		Median concentration of each solvent in mixture (μg/L)
	Denominator is all samples in which solvents were analyzed	Denominator is samples in which one or more solvents were detected	
PCE	2.1	33	4.6
TCE			2.7
TCE	0.9	14	4.2
TCA			7.6
PCE	0.7	11	2.8
TCA			3.9
PCE			4.8
TCE	0.5	8.3	8.7
TCA			7.6
PCE	0	0	NA
Methylene chloride			
TCE	0	0	NA
Methylene chloride			
TCA	0	0	NA
Methylene chloride			
PCE			
TCA	0	0	NA
Methylene chloride			
PCE			
TCE	0	0	NA
Methylene chloride			
TCE			
TCA	0	0	NA
Methylene chloride			
PCE			
TCE	0	0	NA
TCA			
Methylene chloride			

EXPLANATION
- CWS sampled with no detection of one or more solvents
- CWS sampled with detection of one or more solvents

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

Figure 13.   Locations of community water systems (CWSs) that were sampled for methylene chloride, perchloroethene, 1,1,1-trichloroethane, or trichloroethene and where one or more solvents were detected at an assessment level of 0.2 microgram per liter.

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

Figure 14.   Locations of community water systems (CWSs) that were sampled for methylene chloride and where methylene chloride was detected at an assessment level of 0.2 microgram per liter.

EXPLANATION
- CWS sampled with no detection of PCE
- CWS sampled with detection of PCE

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

Figure 15.   Locations of community water systems (CWSs) that were sampled for perchloroethene (PCE) and where PCE was detected at an assessment level of 0.2 microgram per liter.

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

Figure 16.   Locations of community water systems (CWSs) that were sampled for 1,1,1-trichloroethane (TCA) and where TCA was detected at an assessment level of 0.2 microgram per liter.

EXPLANATION
- CWS sampled with no detection of TCE
- CWS sampled with detection of TCE

0   125   250 MILES

0   125   250 KILOMETERS

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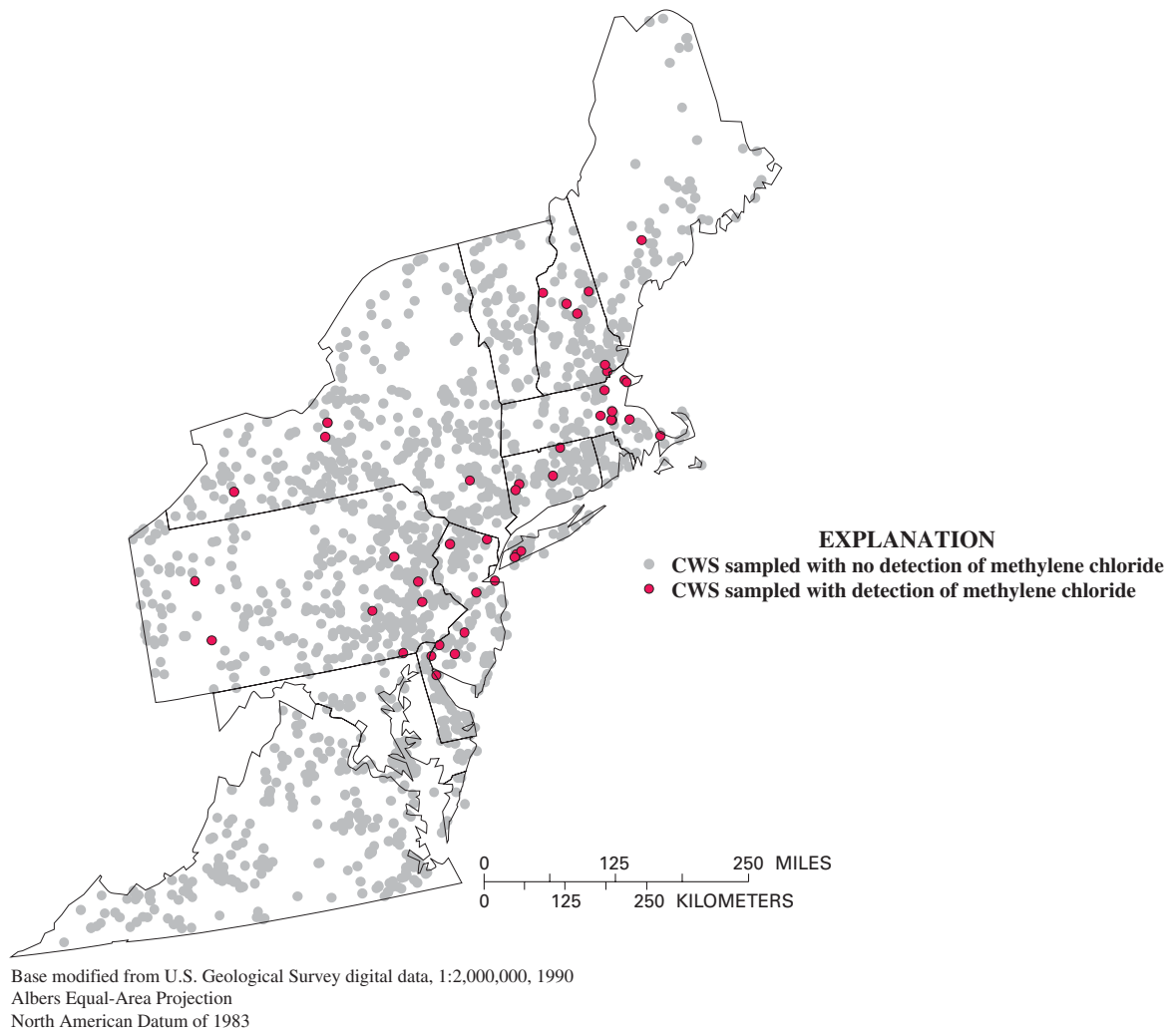Albers Equal-Area Projection
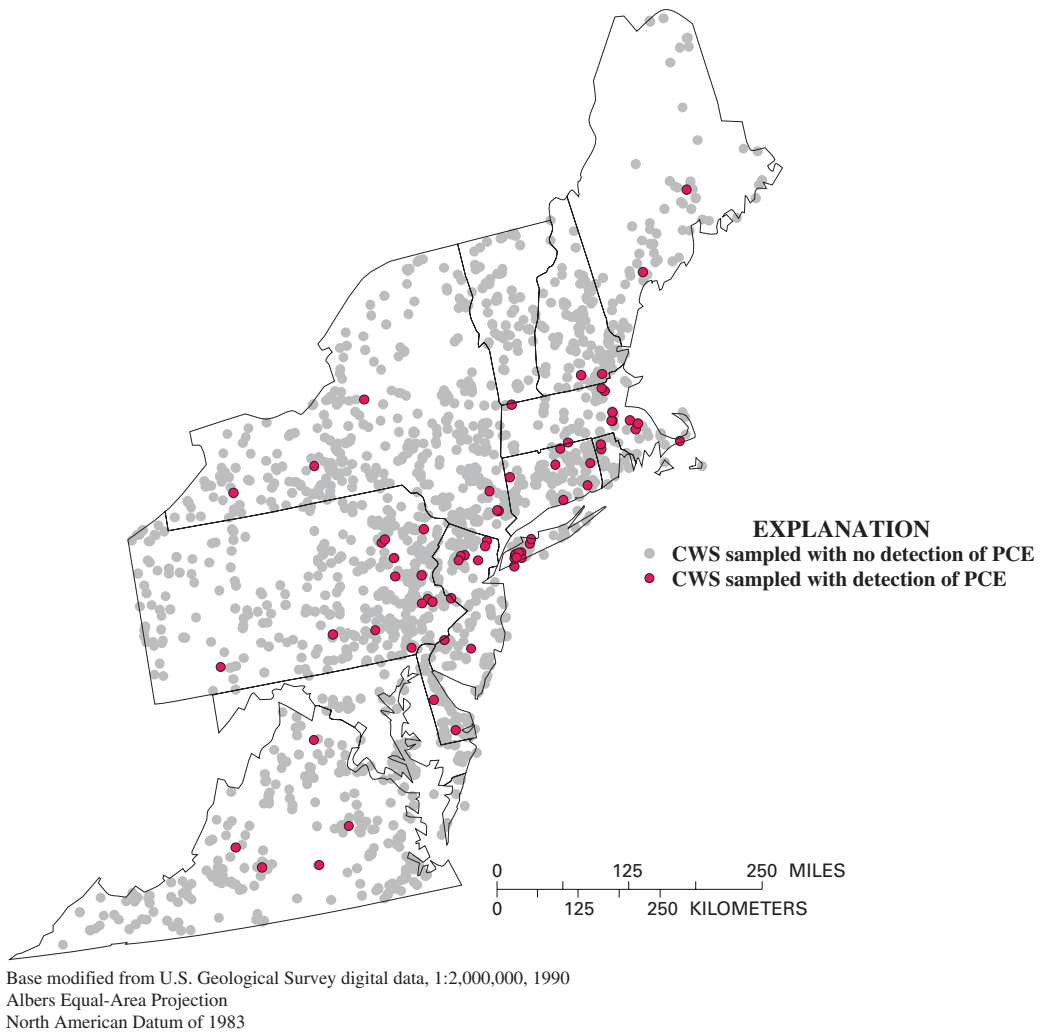North American Datum of 1983

Figure 17.   Locations of community water systems (CWSs) that were sampled for trichloroethene (TCE) and where TCE was detected at an assessment level of 0.2 microgram per liter.
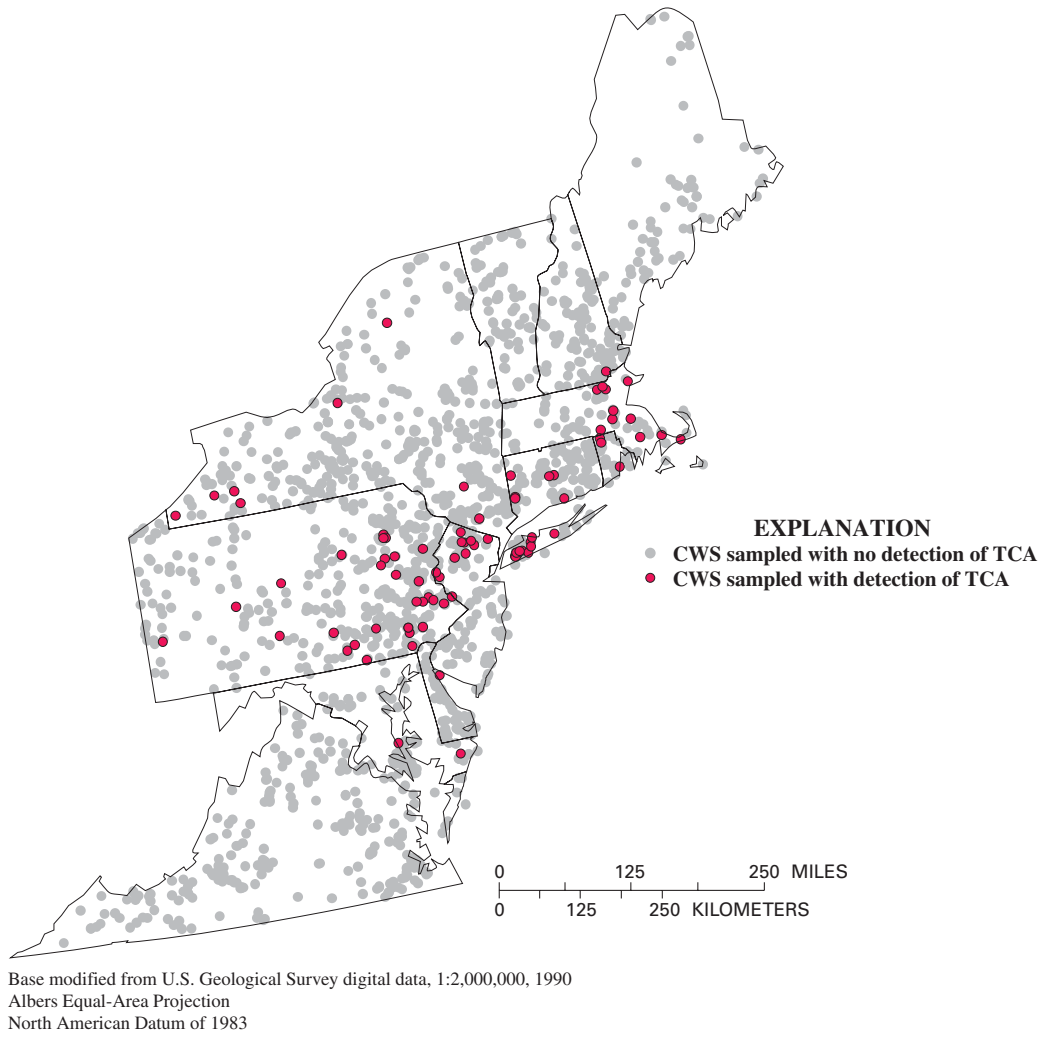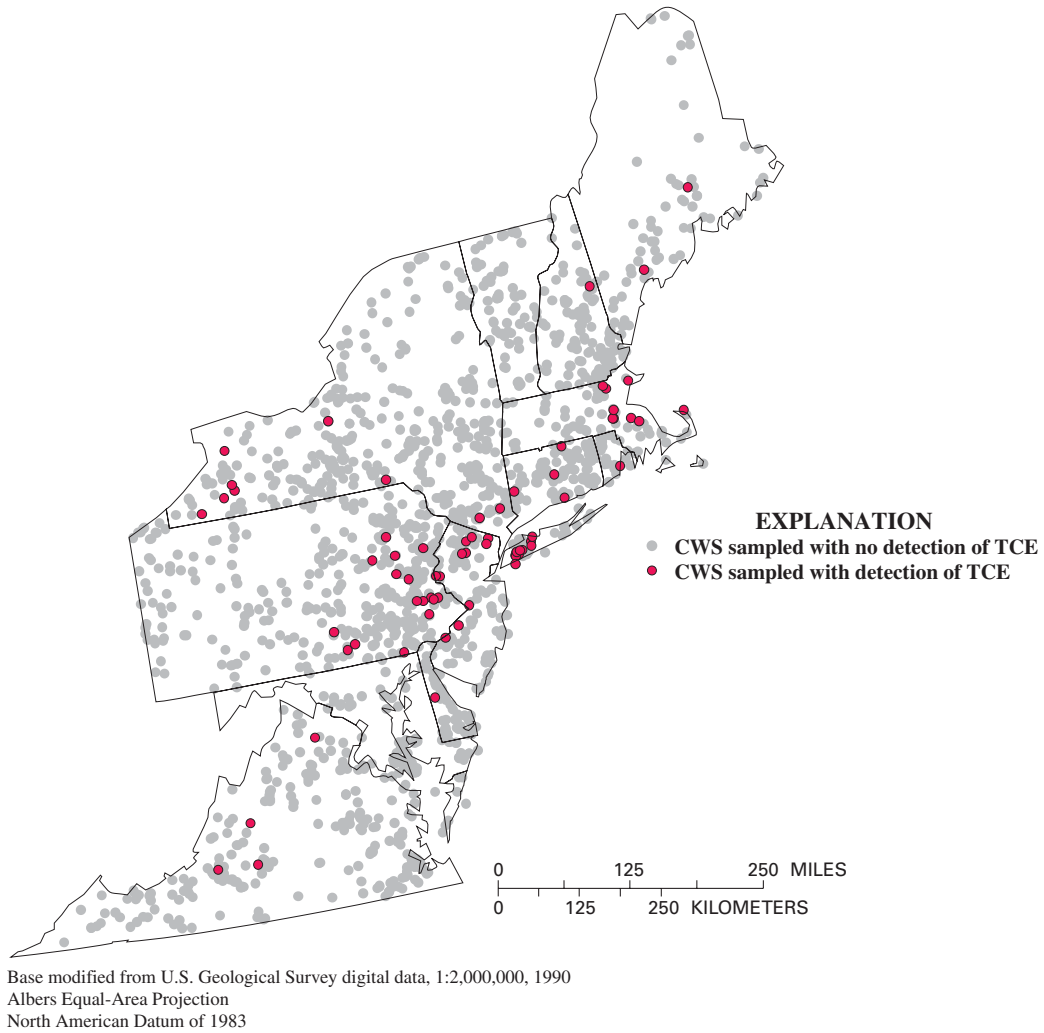
Concentrations of Solvents in Ground Water

At an assessment level of 0.02 µg/L, the four solvents were ranked as follows with respect to the median quantified concentrations of 55 VOCs in ground water nationwide: TCE, 12; PCE, 20; TCA, 27; and methylene chloride, 30 (Appendix 5). Forty-seven of the 55 VOCs had at least one quantified concentration of 0.02 µg/L or greater. The solvents do not have the largest concentrations among the 47 VOCs with quantified concentrations and instead tend to appear near the middle of the rankings. The median quantified concentrations of solvents in ground water were as follows: TCE, 0.12 µg/L; PCE, 0.07 µg/L; TCA, 0.06 µg/L; and methylene chloride, 0.05 µg/L. These values were well below the USEPA MCLs (Appendix 1).

A more complete way to examine the concentrations of solvents in ground water relative to one another is shown in figure 18. The symbols in the graph in figure 18 illustrate quantiles of concentrations of 0.02 µg/L or greater for each solvent. All concentrations less than 0.02 µg/L were assigned a default concentration value of 10^{-4} for plotting.

At an assessment level of 0.02 µg/L, concentrations of PCE were highest followed by TCE, then TCA and finally methylene chloride (fig. 18). It is interesting to note in figure 18 that, although concentrations of TCE were higher than TCA overall, the concentrations of TCA were higher than concentrations of TCE less than about 0.08 µg/L. Because the median laboratory reporting levels for these two compounds using the NWQL low-level method were very similar (table 6), the change in the concentration distributions between TCE and TCA may reflect a true difference in the environmental distribution of concentrations of these two solvents.

Relative to 24 VOCs measured in ground water that have MCLs, the ranking of the four solvents with respect to the frequency of concentrations greater than MCLs in ground water nationwide was as follows: PCE, 1; TCE, 3; and methylene chloride, 9 (Appendix 6). Unlike median quantified concentrations, the frequencies of concentrations greater than MCLs for solvents were higher than most other VOCs, with the exception of TCA, which did not exceed the MCL in samples of ground water.

The frequencies of concentrations of each of the four solvents in ground water that were greater than their MCLs were as follows: PCE, 0.7 percent; TCE, 0.4 percent; methylene chloride, 0.06 percent; and TCA, 0 percent. The numbers of samples in which concentrations were greater than the MCL for each solvent were as follows: PCE, 37; TCE, 20; methylene chloride, 3; and TCA, 0. Table 11 lists the number of concentrations greater than the MCL for each solvent in ground water by well type. For PCE, the majority of samples with concentrations greater than the MCL were in monitoring or other types of wells. For TCE, equal numbers of samples with concentrations greater than the MCL occurred in monitoring or domestic wells compared to public or other types of wells. For methylene chloride, two samples from public wells and one sample from a monitoring well had concentrations that were greater than the MCL.

Figure 18.   Quantiles of concentrations of each of four solvents in ground water at an assessment level of 0.02 microgram per liter.

The median concentrations of solvents in mixtures in ground water are given in table 9. Most concentrations were less than about 2 µg/L. Several concentrations of methylene chloride in mixtures were relatively high because there were few samples with these mixtures, and the concentrations of methylene chloride were high in the samples containing these mixtures. No trend is apparent in the median concentration of solvents in a mixture compared to the frequency of occurrence of the mixture. Also, the median concentration of solvents in mixtures at an assessment level of 0.02 µg/L was about one order of magnitude less than the median concentration of solvents in mixtures at an assessment level of 0.2 µg/L (table 9).

Table 11.   Number of exceedances of MCLs for each solvent in ground water nationwide by well type.

[PCE, perchloroethene; TCE, trichloroethene]

Well type	Solvent		
	PCE	**TCE**	**Methylene chloride**
Public	3	4	2
Domestic	5	6	0
Monitoring	15	6	1
Other	14	4	0
Total	37	20	3

Concentrations of Solvents in Source Water

The four solvents were ranked as follows with respect to the median quantified concentrations of 52 VOCs in source water nationwide: TCA, 3; methylene chloride, 8; TCE, 10; and PCE, 16 (Appendix 7). The assessment level used was 0.2 µg/L, and 40 of the 55 VOCs had at least one quantified concentration of 0.2 µg/L or greater. Unlike the ground-water samples, solvents in source-water samples were in the upper one-half of the rankings with respect to the median of quantified concentrations of 40 VOCs with at least one quantified concentration. The median quantified concentrations of solvents in source water were as follows: TCA, 4.4 µg/L; methylene chloride, 1.7 µg/L; TCE, 1.5 µg/L; and PCE, 0.9 µg/L. Although these median values are less than MCLs (Appendix 1), the median values for methylene chloride and TCE are only about three times lower.

Figure 19 shows the quantiles of concentrations of each solvent in source water at an assessment level of 0.2 µg/L. Values less than 0.2 µg/L were assigned a default value of 10^{-4} for plotting. Based on the quantiles, the concentrations of PCE in source water generally were highest followed by TCE, TCA, and methylene chloride. However, between about 0.5 and 1.0 µg/L, the concentrations of TCE were higher than the concentrations of PCE. The highest concentration of a solvent in source water was for TCE.

Relative to 23 VOCs measured in source water that have MCLs, the rankings of the four solvents with respect to the frequency with which concentrations were greater than their

MCLs in source water nationwide was as follows: PCE, 1; TCE, 2; TCA, 6; and methylene chloride, 6 (Appendix 8). Neither TCA nor methylene chloride had concentrations greater than the MCL in any samples of source water. In source water, only five VOCs had concentrations greater than MCLs, and two of them were solvents with PCE ranking first and TCE ranking second.

The frequencies of concentrations that were greater than their MCLs for each of the four solvents in source water were as follows: PCE, 1.1 percent; TCE, 0.9 percent; TCA, 0 percent; and methylene chloride, 0 percent. The numbers of samples in which concentrations were greater than the MCL for each solvent were as follows: PCE, 6; TCE, 5; TCA, 0; and methylene chloride, 0. For PCE, the locations of public wells from which samples had concentrations greater than the MCL were as follows: California, 2; New York, 2; Ohio, 1; and Pennsylvania, 1. For TCE, the locations of public wells from which samples had concentrations greater than the MCL were as follows: New York, 2; Iowa, 1; California, 1; and Pennsylvania, 1.

The concentrations of solvents in mixtures in source water are given in table 10. In contrast to ground-water samples, most concentrations of solvents in mixtures in source-water samples were greater than 2 µg/L. No trend was apparent in the median concentration of solvents in a mixture compared to the frequency of occurrence of the mixture (table 10).

Concentrations of Solvents in Drinking Water

The four solvents were ranked as follows with respect to the median quantified concentrations of 51 VOCs in drinking water: TCE, 8; PCE, 11; TCA, 25; and methylene chloride, 31 (Appendix 9). Because the drinking-water data consisted of multiple samples from each CWS, the median value of quantified VOC concentrations for each CWS was the median of all quantified VOC concentrations from that CWS. The assessment level used was 0.2 µg/L, and 44 of the 55 VOCs had at least one quantified concentration of 0.2 µg/L or greater. With respect to median quantified concentrations, solvents in drinking water ranked in the upper one-half of the 49 VOCs with at least one quantified concentration, with the exception of TCA and methylene chloride. The median quantified concentrations of solvents in source water were as follows: TCE, 1.5 µg/L; PCE, 1.4 µg/L; TCA, 1 µg/L; and methylene chloride, 1 µg/L. Although these median values were less than MCLs, the median values for PCE and TCE were only about three times lower.

Figure 20 shows the quantiles of concentrations of each solvent in drinking water at an assessment level of 0.2 µg/L. Concentrations of TCA in drinking water were highest followed by PCE, TCE, and methylene chloride; however, the concentrations of TCA, PCE, and TCE were nearly equal. The quantified concentration for each CWS was the median of quantified concentrations if multiple quantified concentrations from a CWS were available. Values less than 0.2 µg/L were given a default concentration value of 10^{-4} for plotting.

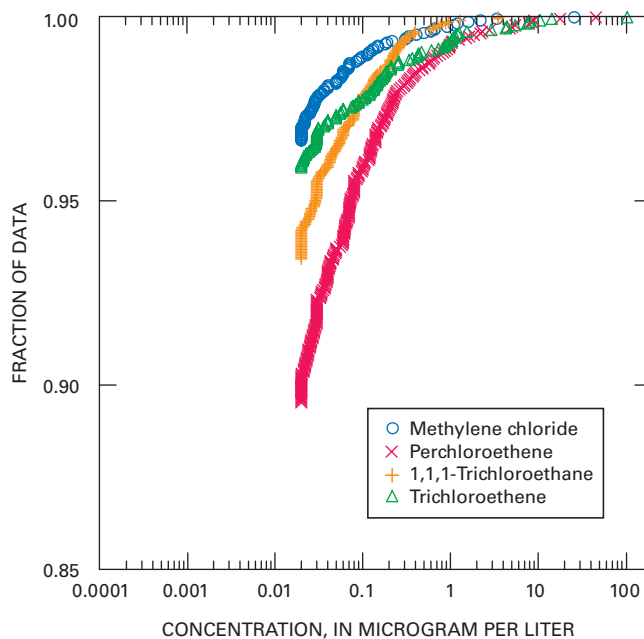**Figure 19.**   Quantiles of concentrations of each of four solvents in source water at an assessment level of 0.2 microgram per liter.
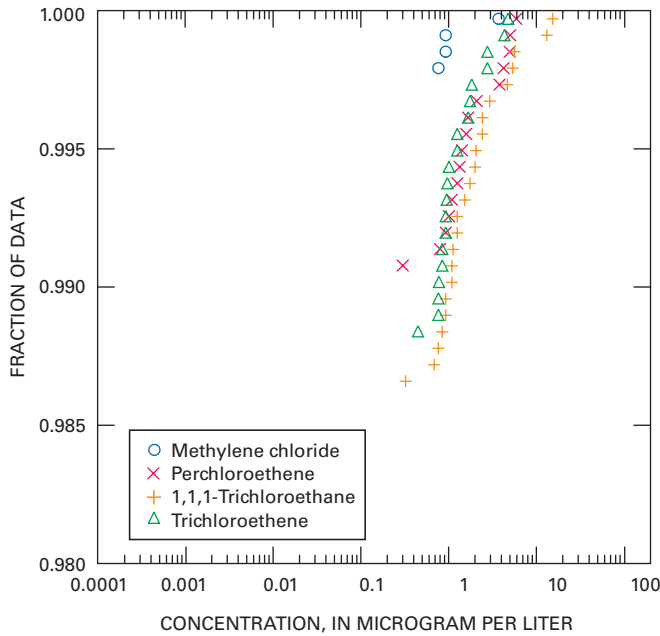
Figure 20.   Quantiles of concentrations of each of four solvents in drinking water at an assessment level of 0.2 microgram per liter.

figure 21. The detection frequencies shown in figure 21 were computed using an assessment level of 0.2 µg/L. Because the drinking-water data were limited to 12 Northeast and Mid-Atlantic States, the data for ground water and source water also were constrained to these areas to make the comparisons of detection frequencies with drinking water most equitable.

The detection frequency of one or more solvents was higher in source water at about 13 percent and lower in both ground water and drinking water at about 11 percent. However, the detection frequencies of solvents in each data set were similar and vary by less than 2 percent. The differences in detection frequencies between any of the data sets were not significant at the 95-percent confidence interval. When examined nationwide, the detection frequencies of one or more solvents were about 7 percent for ground water and about 6 percent for source water. The differences in nationwide detection frequencies of one or more solvents between ground water and source water were not significant at the 95-percent confidence interval.

Relative to the 24 VOCs measured in drinking water that have MCLs, the ranking of the four solvents with respect to the frequency with 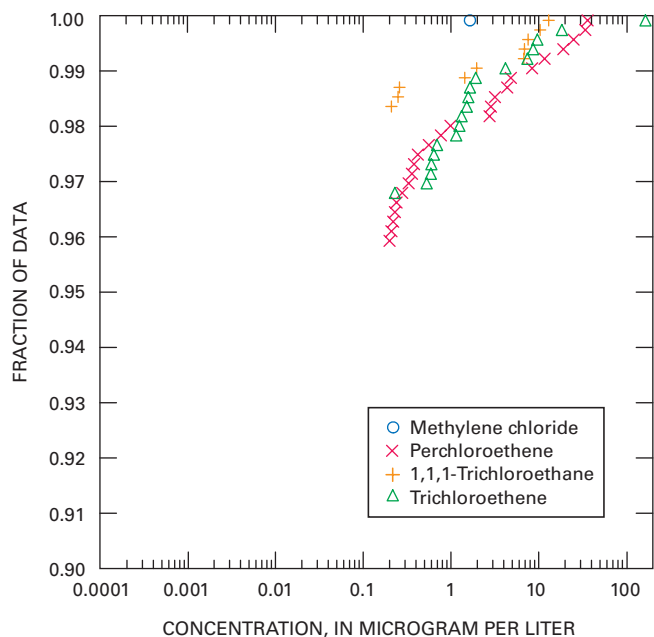which concentrations were greater than their MCLs in drinking water was as follows: PCE, 1; TCE, 2; methylene chloride, 6; and TCA, 13 (Appendix 10). In this case, the highest concentration from each CWS was selected for comparison to MCLs if multiple samples of quantified concentrations of solvents were available. TCA concentrations were not greater than the MCL in any samples from any CWS.

The frequencies of concentrations of each of the four solvents in drinking water that were greater than their MCLs were as follows: PCE, 1.6 percent; TCE, 1.2 percent; methylene chloride, 0.2 percent; and TCA, 0 percent. The numbers of CWSs in which concentrations were greater than the MCL for each solvent were as follows: PCE, 26; TCE, 20; methylene chloride, 4; and TCA, 0. For PCE, the majority of concentrations greater than the MCL occurred in New York, Pennsylvania, and Massachusetts. For TCE, the vast majority of concentrations greater than the MCL occurred in New York. For methylene chloride, the locations of CWSs from which samples had concentrations greater than the MCL were as follows: Massachusetts, 2; New York, 1; and New Jersey, 1.

Comparisons of Solvent Occurrence and Concentrations Between Ground Water, Source Water, and Drinking Water

The occurrence of any one or more of the four solvents in ground water, source water, and drinking water is illustrated in

Figure 21.   Detection frequencies of one or more solvents in ground water, source water, and drinking water in 12 Northeast and Mid-Atlantic States at an assessment level of 0.2 microgram per liter.

The detection frequencies of each individual solvent in ground water, source water, and drinking water are illustrated in figure 22. The detection frequencies were computed using an assessment level of 0.2 µg/L. Because the drinking-water data were limited to 12 Northeast and Mid-Atlantic States, the data for ground water and source water also were constrained to these areas to make the comparisons of detection frequencies with drinking water most equitable.

The detection frequency of TCA was highest in ground water followed by PCE, TCE, and methylene chloride. In source water, the detection frequency of PCE was highest, followed by TCE, TCA, and methylene chloride. In drinking water, the detection frequency pattern of individual solvents followed that of ground water with TCA being the highest followed by PCE, TCE, and methylene chloride.

The results of Pearson's chi-square tests of independence between data sets for detection frequencies of individual solvents in 12 Northeast and Mid-Atlantic States are shown in table 12. The only difference in detection frequencies at the 95-percent confidence interval that was significant was the difference in detection frequencies of methylene chloride between ground water and drinking water. The detection

frequency of methylene chloride was higher in drinking water compared to ground water.

Table 12. Results of Pearson's chi-square tests comparing detection frequencies of individual solvents between data sets at an assessment level of 0.2 microgram per liter.

[Bolded *p*-value indicates significance at $\alpha = 0.05$. Data limited to 12 Northeast and Mid-Atlantic States. PCE, perchloroethene; TCA, 1,1,1-trichoroethane; TCE, trichoroethene]

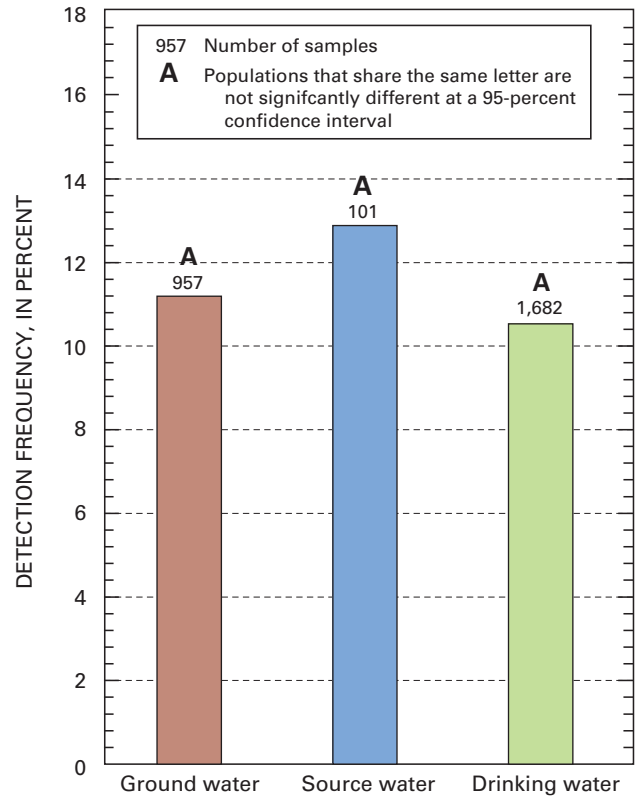| Comparison | *p*-value | | | |
	Methylene chloride	PCE	TCA	TCE
Ground water and source water	0.6387	0.4427	0.6213	0.4185
Source water and drinking water	.1901	.1015	.8737	.2416
Ground water and drinking water	**.0073**	.0872	.367	.5366
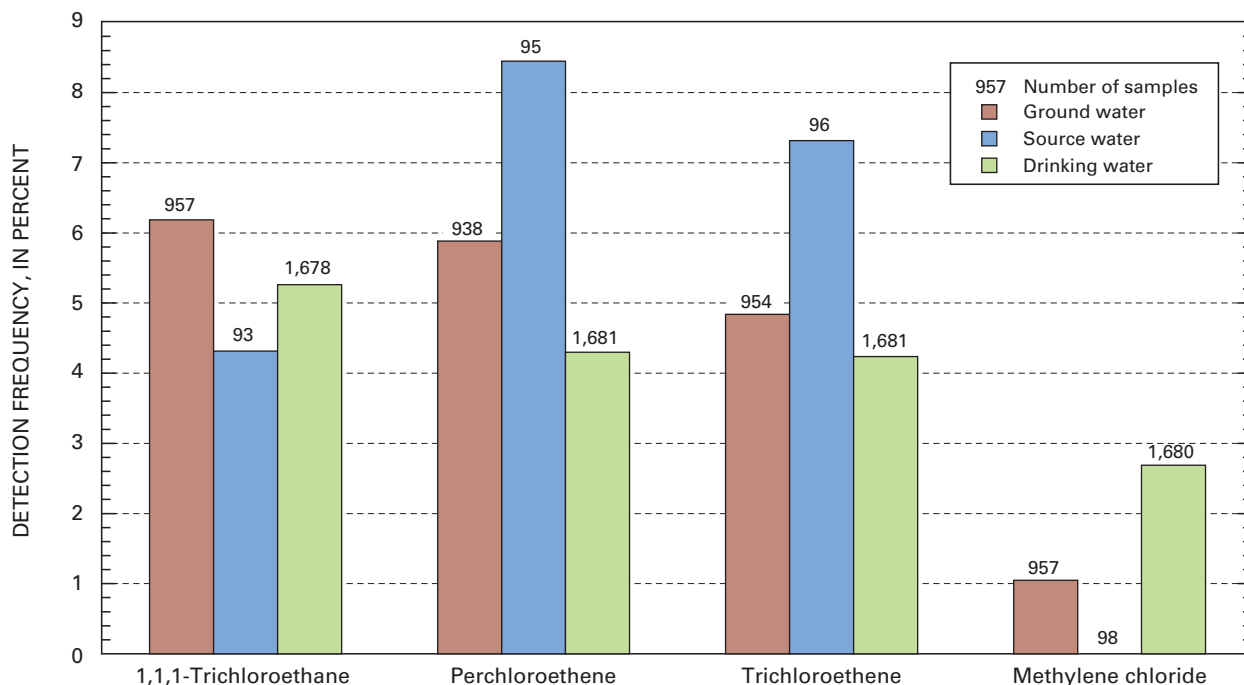
Figure 22. Detection frequencies of individual solvents in ground water, source water, and drinking water in 12 Northeast and Mid-Atlantic States at an assessment level of 0.2 microgram per liter.

The detection frequencies of individual solvents nationwide and at an assessment level of 0.2 μg/L are shown in figure 23. Only data from ground water and source water were available nationwide. The detection frequencies of TCE and methylene chloride had the same pattern nationwide as compared to the 12 Northeast and Mid-Atlantic States, with TCE having a higher detection frequency in source water and methylene chloride having a higher detection frequency in ground water. Detection frequencies were not significantly different between ground water and source water for any solvent at the 95-percent confidence interval.

Table 13 lists the nationwide detection frequency ranking of each solvent relative to a suite of 51 to 55 VOCs analyzed in each data source. A sum of the ranks also is given in this table. The assessment level for computing detection frequencies was 0.2 μg/L. Based on a sum of the ranks of each solvent by data set, PCE is the most frequently occurring of the four solvents in ground water, source water, or drinking water followed by TCE, TCA, and methylene chloride.

The nationwide detection frequencies of individual solvents also were examined in ground water by land use (figs. 4 and 5). Table 14 gives the results of Pearson's chi-square tests of independence for comparisons of the nationwide detection frequencies of individual solvents by land use at an assessment level of 0.2 μg/L. Mixed land use refers to areas

sampled in the aquifer studies. Differences in detection frequencies at the 95-percent confidence interval were significant in every land-use comparison for both PCE and TCE. No significant differences were found between detection frequencies by land use for methylene chloride. For TCA, differences between detection frequencies were significant in every land comparison except mixed land use compared to agricultural land use.

Table 13. Ranking of occurrence of solvents among a suite of VOCs in ground water, source water nationwide and drinking water in 12 Northeast and Mid-Atlantic States based on detection frequencies at an assessment level of 0.2 microgram per liter.

[PCE, perchloroethene; TCA, 1,1,1-trichoroethane;; TCE, trichoroethene]

| Data set | Solvent ranking | | | |
	Methylene chloride	PCE	TCA	TCE
Ground water	13	3	5	4
Source water	28	6	10	7
Drinking water	11	7	6	8
Rank sum	**52**	**16**	**21**	**19**
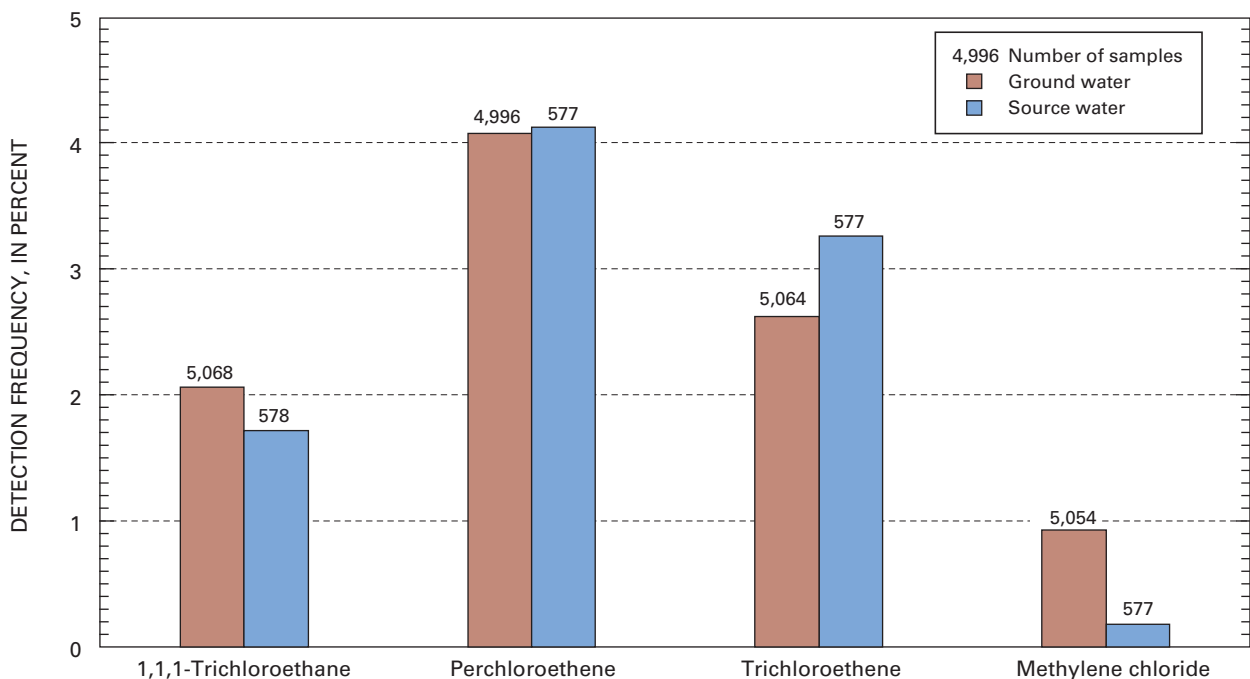
Figure 23. Detection frequencies of individual solvents in ground water and source water, nationwide at an assessment level of 0.2 microgram per liter.

Table 14.   Results of Pearson's chi-square tests comparing nationwide detection frequencies of individual solvents by land use at an assessment level of 0.2 microgram per liter.

[Bolded *p*-value indicates significance at $\alpha = 0.05$. PCE, perchloroethene; TCA, 1,1,1-trichoroethane; TCE, trichoroethene]

Comparison	*p*-value			
	Methylene chloride	**PCE**	**TCA**	**TCE**
Mixed[1] land use and urban[2] land use	0.5497	**0**	**0**	**0.0002**
Mixed[1] land use and agricultural[3] land use	.9491	**0**	.0559	**.0001**
Agricultural[3] land use and urban[2] land use	.6565	**0**	**0**	**0**

[1]Data from National Water-Quality Assessment (NAWQA) aquifer studies.

[2]Data from NAWQA shallow ground-water studies in urban areas.

[3]Data from NAWQA shallow ground-water studies in agricultural areas.

Quantiles of concentrations of methylene chloride, PCE, TCA, and TCE in ground water, source water, and drinking water are illustrated in figures 24–27, respectively. All concentrations were compared at an assessment level of 0.2 µg/L. The data for ground water and source water were limited to 12 Northeast and Mid-Atlantic States in order to make the comparisons with drinking water more equitable. For drinking water, the quantified concentration for each CWS was the median quantified concentration by CWS when multiple quantified concentrations were available.

Table 15 gives the results of Kolmogorov-Smirnov tests comparing the distributions of concentrations of each solvent in ground water, source water, and drinking water in the 12 Northeast and Mid-Atlantic States. None of the comparisons of the distributions of the concentrations were significantly different at the 95-percent confidence interval.
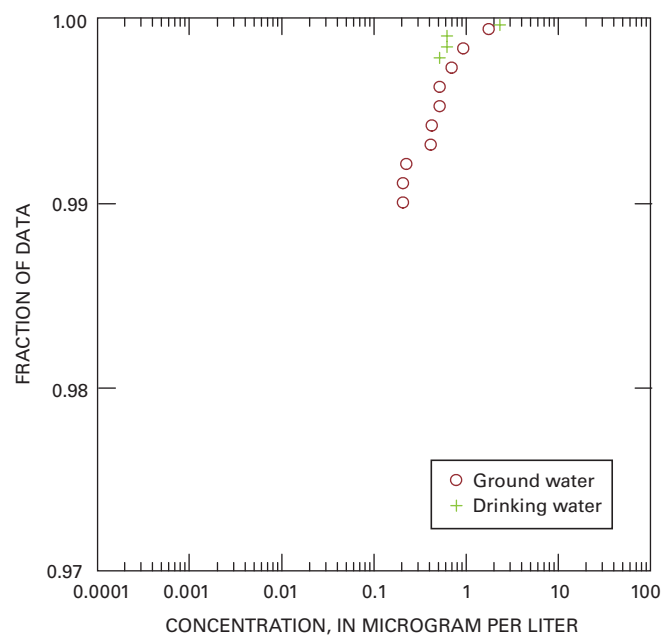
Figure 24.   Quantiles of concentrations of methylene chloride in ground water and drinking water in 12 Northeast and Mid-Atlantic States at an assessment level of 0.2 microgram per liter.
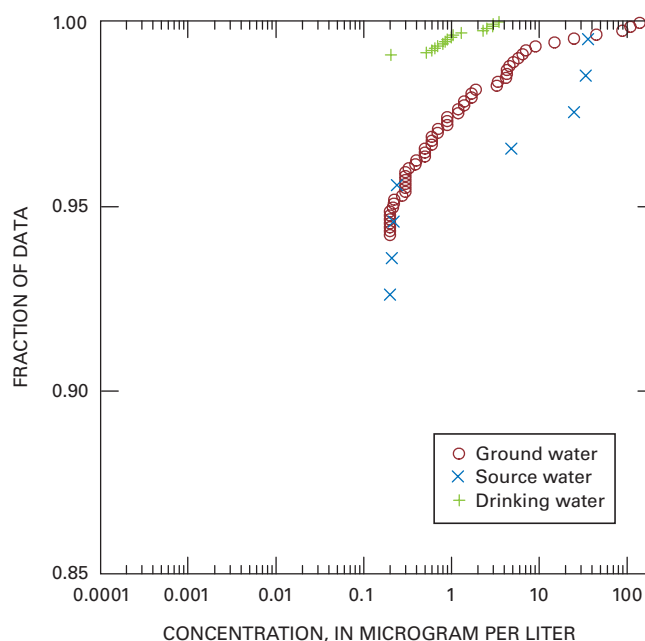
Figure 25.   Quantiles of concentrations of perchloroethene in ground water, source water, and drinking water in 12 Northeast and Mid-Atlantic States at an assessment level of 0.2 microgram per liter.
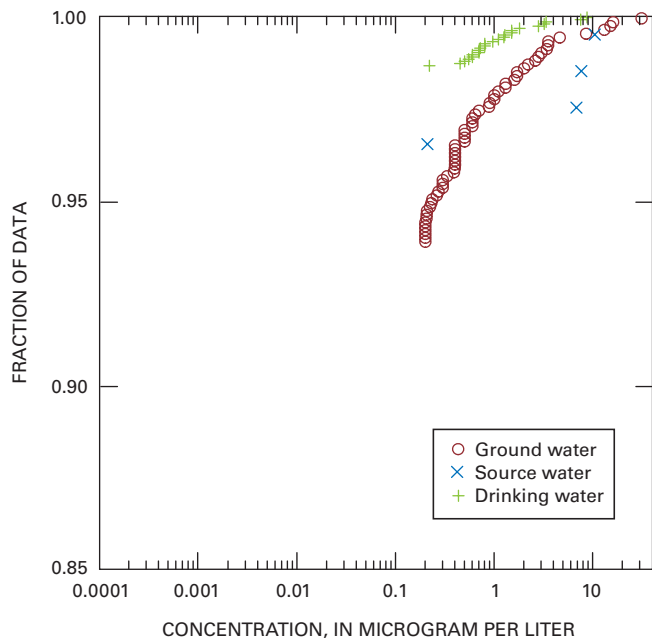
Figure 26. Quantiles of concentrations of 1,1,1-trichloroethane in ground water, source water, and drinking water in 12 Northeast and Mid-Atlantic States at an assessment level of 0.2 microgram per liter.
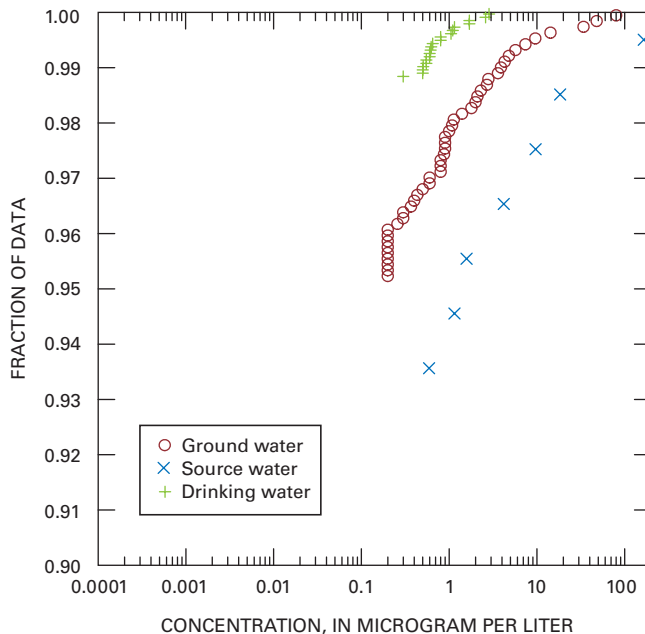
Figure 27. Quantiles of concentrations of trichloroethene in ground water, source water, and drinking water in 12 Northeast and Mid-Atlantic States at an assessment level of 0.2 microgram per liter.

Table 15. Results of Kolmogorov-Smirnov tests comparing the distributions of concentrations of solvents in ground water, source water, and drinking water.

[Data limited to 12 Northeast and Mid-Atlantic States. PCE, perchloroethene; TCA, 1,1,1-trichoroethane; TCE, trichoroethene]

Comparison	*p*-value			
	Methylene chloride	PCE	TCA	TCE
Ground water and source water	1	1	1	0.998
Source water and drinking water	1	1	1	1
Ground water and drinking water	1	.19	.266	.618

Table 16 lists the rank of each solvent in ground water, source water, and drinking water with respect to the frequency of concentrations greater than the MCLs relative to other VOCs. Table 16 also includes a rank sum for each solvent indicating the relative frequency of concentrations greater than MCLs for each solvent. The rankings for ground water and source water were for all data nationwide while the rankings for drinking water were for CWSs in 12 Northeast and Mid-Atlantic States. As indicated by their rank sum, in ground water, source water, and drinking water, the VOCs that most frequently had concentrations greater than the MCL were PCE and TCE. They were followed by methylene chloride and TCA, which had concentrations greater than the MCLs much less frequently (table 16).

The frequency of concentrations greater than the MCLs for each solvent in each data set is shown in figure 28. The data for ground water and source water were limited to 12 Northeast and Mid-Atlantic States in order to make the comparisons to drinking water more equitable. For drinking-water data, the highest quantified concentration of each solvent in each CWS was selected when multiple concentrations were available. The results of Pearson's chi-square tests of independence comparing frequencies of concentrations greater than the MCLs for each individual solvent between data sets are given in table 17.

Table 16. Rank of frequency of concentrations of solvents greater than their Maximum Contaminant Levels (MCLs) compared to other volatile organic compounds (VOCs) nationwide in ground water and source water, and in drinking water in 12 Northeast and Mid-Atlantic States.

[PCE, perchloroethene; TCA, 1,1,1-trichoroethane; TCE, trichoroethene]

| Data set | Number of VOCs that exceeded an MCL | Solvent exceedance frequency ranking | | | |
		Methylene chloride	PCE	TCA	TCE
Ground water	11	9	1	[1]12	3
Source water	5	[1]6	1	[1]6	2
Drinking water	12	6	1	[1]13	2
Rank sum		**21**	**3**	**31**	**7**

[1]Frequency of exceedance of MCLs was 0 percent.

For both ground water and drinking water, the frequencies of concentrations greater than the MCL were highest for PCE followed by TCE. However, the frequencies of concentrations greater than the MCL for PCE in both ground water or drinking water were fairly low at 1.6 percent in drinking water and 1.2 percent in ground water. In source water, the frequencies of concentrations greater than the MCL for PCE and TCE were

highest and were identical at 3 percent. The concentrations of TCA were not greater than the MCL in any samples from any data set, and methylene chloride was greater than the MCL only in drinking water and only in four CWSs. None of the frequencies of concentrations greater than the MCL of any solvent in any of the comparisons between data sets were significantly different (table 17).

Table 17. Results of Pearson's chi-square tests comparing frequencies of concentrations greater than the Maximum Contaminant Levels for individual solvents between data sets.

[Bolded *p*-value indicates significance at α = 0.05). Data limited to 12 Northeast and Mid-Atlantic States.
PCE, perchloroethene; TCA, 1,1,1-trichoroethane; TCE, trichoroethene]

| Comparison | *p*-value | | | |
	Methylene chloride	PCE	TCA	TCE
Ground water and source water	1	0.3008	1	0.0957
Source water and drinking water	.5496	.4881	1	.2775
Ground water and drinking water	.322	.5452	1	.3597
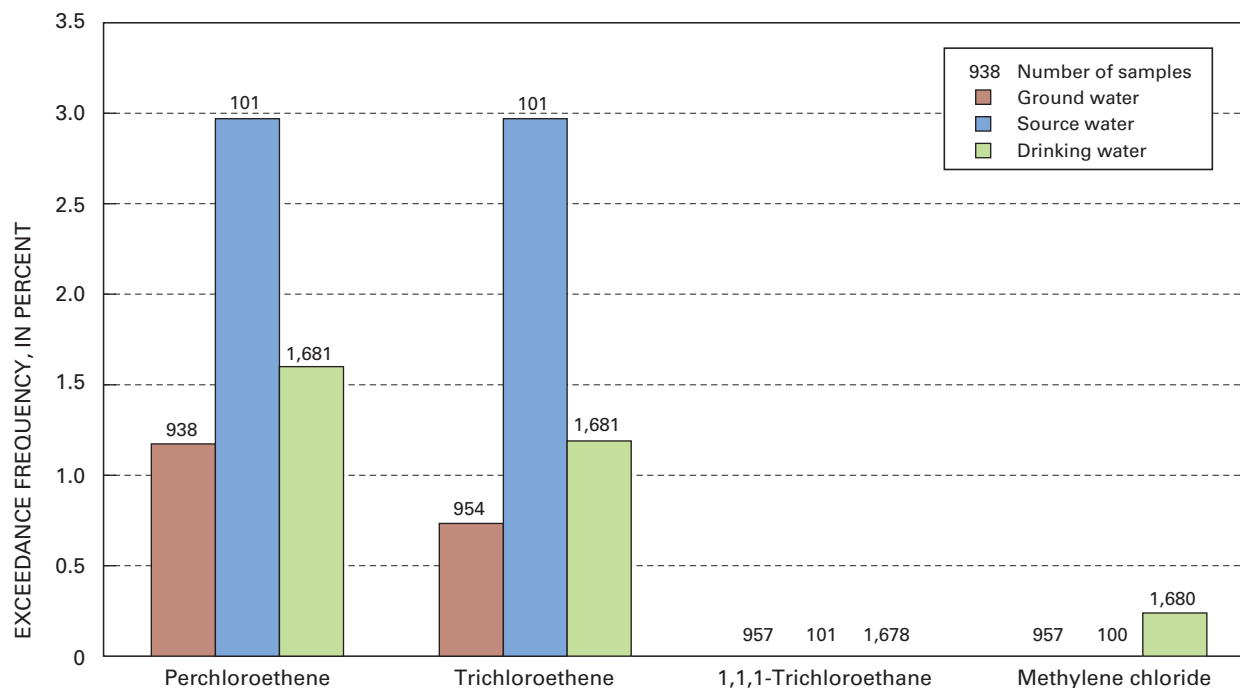
Figure 28. Frequencies of concentrations greater than the Maximum Contaminant Levels by individual solvents in ground water, source water, and drinking water in 12 Northeast and Mid-Atlantic States at an assessment level of 0.2 microgram per liter.

The frequencies of concentrations of individual solvents greater than the MCL also were examined in ground water nationwide by land use (fig. 29). The results of Pearson's chi-square tests of independence comparing frequencies of concentrations of individual solvents greater than the MCLs nationwide between land uses are given in table 18.

PCE concentrations were greater than the MCL most frequently in urban and mixed land-use areas. The frequency of concentrations greater than the MCL for TCE were nearly the same in urban and mixed land-use areas and lower than PCE. No concentrations of PCE, TCA, or TCE were greater than the MCL in agricultural land-use areas. The concentrations of TCA were not greater than the MCL in any land-use area, and the concentrations of methylene chloride greater than the MCL were less than 1 percent in mixed and agricultural land-use areas. The frequency of concentrations greater than the MCL for PCE were higher in urban land-use areas than in either mixed or agricultural land-use areas, and each difference was statistically significant (table 18). No other comparisons of frequencies of concentrations greater than the MCL were significantly different.

Table 18. Results of Pearson's chi-square tests comparing frequencies of concentrations greater than the Maximum Contaminant Levels for individual solvents in ground water between land uses.

[Bolded *p*-value indicates significance at $\alpha = 0.05$). PCE, perchloroethene; TCA, 1,1,1-trichloroethane; TCE, trichoroethene]

Comparison	*p*-value			
	Methylene chloride	PCE	TCA	TCE
Mixed[1] land use and urban[2] land use	0.8439	**0.0085**	1	0.8211
Mixed[1] land use and agricultural[3] land use	.9814	.0558	1	.1374
Agricultural[3] land use and urban[2] land use	.9382	**.0013**	1	.1789

[1] Data from National Water-Quality Assessment (NAWQA) aquifer studies.

[2] Data from NAWQA shallow ground-water studies in urban areas.

[3] Data from NAWQA shallow ground-water studies in agricultural areas.
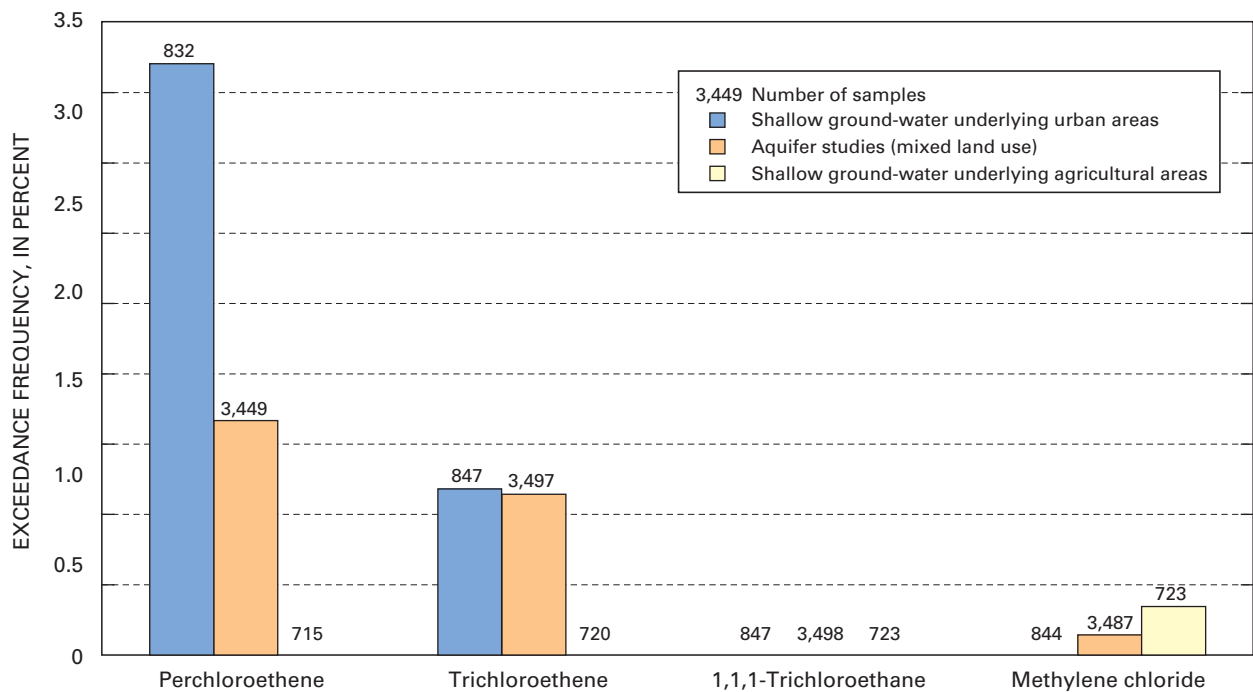

Figure 29. Frequencies of concentrations greater than the Maximum Contaminant Levels in ground water from National Water-Quality Assessment studies by individual solvent and land use.

Associations of Solvents with Hydrogeologic and Anthropogenic Variables

The results of the logistic regression analyses for one or more of the four solvents and individual solvents are summarized in table 19. Table 19 lists the variables that were significantly associated with one or more solvents or individual solvents, the coefficient for each association in the logistic regression equation, the standardized coefficient, and the Hosmer-Lemeshow statistic *p*-value. Standardized coefficients greater than 0.1 were considered to be strongly associated with the probability of occurrence of solvents and are highlighted in gray in table 19.

Variables Associated With One or More Solvents

The probability of detecting one or more of the four solvents was most strongly associated with sand content of soil (table 19). The probability of detecting one or more solvents increased as the sand content of the soil decreased. It might be assumed that a decrease in sand content of the soil would decrease the permeability of the soil and thereby limit the downward movement of contaminants like solvents to ground water. However, in the vadose zone at low pressure head or water content, the unsaturated hydraulic conductivity of a fine-textured soil may be greater than that of a coarse soil (Stephens, 1996).

Over the range of pressure heads and water contents likely to be encountered in the vadose zone, the unsaturated hydraulic conductivity of a soil can vary greatly, and the variability is even greater between soils of different textures (Stephens, 1996). In addition, soil texture properties like sand content can be used to estimate soil hydraulic properties indicating that a relation exists between texture and hydraulic characteristics (Schaap and Leij, 1998). It is likely that sand content of soil is a surrogate for another soil property, such as unsaturated hydraulic conductivity of the soil zone, that would be expected to strongly influence the occurrence of solvents in ground water.

The probability of detecting one or more solvents also was strongly associated with the percent of urban land and population density in proximity to the wells (table 19). The probability of detecting one or more solvents increased as either percent urban land use or population density increased. Urban land use and population density represent sources of solvents to ground water and are aggregate surrogate variables. Although they do not represent specific sources of solvents to ground water, as both of these variables increase there is an increase in multiple potential sources of solvents, such as commercial, industrial, and transportation activities.

The probability of detecting one or more solvents also was strongly associated with dissolved-oxygen content of ground water (table 19). The probability of detecting one or more solvents increased as dissolved oxygen of ground-water content increased. Dissolved oxygen is a key factor in processes that determine the fate of solvents in ground water, primarily biodegradation. Solvents are known to biodegrade under anoxic conditions. In oxic ground water, less biodegradation occurs (other than by co-metabolism), and therefore a higher concentration of solvents can remain in solution. Consequently, the probability of detecting solvents should be higher in oxic ground water compared to anoxic ground water. In this case, oxic and anoxic conditions in ground water are simply defined as conditions of relatively high and relatively low dissolved oxygen.

The probability of detecting one or more solvents was weakly associated with depth to the top of the screened interval in the wells, the number of Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) sites within 1 km of the wells, and the number of septic systems within 1 km of the wells (table 19). The probability of detecting one or more solvents decreased as depth to the top of the screened interval increased. As depth to the top of the screened interval increases, the time required for a solvent to reach the screened interval by movement through the vadose and saturated zones also increases, provided there is no short cutting of traveltime to the screened interval (Moran and others, 2002). This increased time allows for increased attenuation of solvent concentrations through natural loss processes such as biodegradation, sorption, dispersion, and volatilization.

The probability of detecting one or more solvents increased as either the number of CERCLA sites or the number of septic systems in proximity to the wells increased (table 19). These two terms represent sources of solvents to ground water. CERCLA sites are facilities that have experienced releases of toxic or hazardous substances and that the Federal government has indicated are a priority for clean up. CERCLA sites may be sources of solvents to ground water if solvents were released at the site. Likewise, septic systems could be a source of solvents to ground water because many types of household products contain solvents and it is likely that these are disposed of in septic systems. However, the number of septic systems within 1 km of the wells was the weakest variable associated with the probability of occurrence of solvents in ground water, and thus, septic systems may not be the primary source for solvents in ground water but may be only a contributing source in some cases (table 19).

Table 19. Hydrogeologic and anthropogenic variables that were associated with the probability of occurrence of one or more solvents or individual solvents in ground water.

[km, kilometer; RCRA, Resource Conservation and Recovery Act; CERCLA, Comprehensive Environmental Response, Compensation, and Liability Act; PCE, perchloroethene; TCA, 1,1,1-trichoroethane; TCE, trichoroethene]

Solvent	Associated variables (gray shading indicates a weak[1] association)	Type of variable	Unstandardized coefficient in logistic regression equation	Standardized coefficient	Hosmer-Lemeshow statistic *p*-value
One or more solvents	Sand content of soil	Transport	-0.026	-0.22	
		Source	1.544	0.21	
	Dissolved oxygen	Fate	0.134	0.16	
	Population density	Source	0.303	0.12	0.714
	Depth to top of screened interval	Transport	-0.001	-0.06	
	CERCLA sites within 1 km	Source	0.917	0.05	
	Septic systems within 1 km	Source	0.004	0.05	
Methylene chloride	Population density	Source	0.614	0.11	
	Bulk density of soil	Transport	3.675	0.06	
	Sand content of soil	Transport	-0.016	-0.06	0.093
	Urban land use	Source	-0.847	-0.05	
	Median year of home construction	Source	-0.018	-0.03	
PCE	Urban land use	Source	2.165	0.28	
		Transport	-0.028	-0.22	
	Dissolved oxygen	Fate	0.137	0.16	
	Soil erodibility	Transport	-4.575	-0.15	0.160
	RCRA sites within 1 km	Source	0.027	0.06	
	Depth to top of screened interval	Transport	-0.001	-0.05	
	Septic systems within 1 km	Source	0.003	0.04	
TCA	Dissolved oxygen	Fate	0.230	0.20	
		Source	1.461	0.14	
	Population density	Source	0.456	0.13	
	Depth to top of screened interval recharge	Transport	-0.003	-0.12	0.174
	Recharge	Transport	0.003	0.11	
	CERCLA sites within 1 km	Source	1.043	0.04	
	Septic systems within 1 km	Source	0.003	0.03	
TCE	Population density	Source	1.139	0.26	
	Dissolved oxygen	Fate	0.121	0.08	
	RCRA sites within 1 km	Source	0.035	0.04	0.133
	CERCLA sites within 1 km	Source	0.871	0.03	
	Casing diameter	Transport	0.033	0.03	

[1]Weak associations are those with a standardized coefficient of less than 0.1.

Variables Associated With Individual Solvents

The probability of detecting methylene chloride in ground water was strongly associated with population density (table 19). As population density increased, the probability of detecting methylene chloride increased. This variable represents sources of methylene chloride to the environment and is an aggregate surrogate variable. The probability of detecting methylene chloride in ground water was weakly associated with bulk density of the soil, sand content of the soil, urban land use, and median year of home construction within 1 km of the wells (table 19). These terms represent source and transport mechanisms in the environment. Both bulk density of the soil and soil sand content likely are surrogates for another soil property such as saturated or unsaturated hydraulic conductivity of the soil zone. In fact, saturated and unsaturated hydraulic conductivity can be estimated from soil data such as soil texture and bulk density (Schaap and Leij, 1998). Median year of home construction is a surrogate variable for source of solvents to ground water from domestic activities and possibly from private septic systems, with older homes having a greater likelihood of contributing solvents to ground water.

The probability of detecting PCE was most strongly associated with urban land use (table 19). The probability of detecting PCE increased as percent urban land use around the wells increased. This variable represents sources of PCE to the environment and is an aggregate surrogate variable. The probability of detecting PCE also was strongly associated with sand content of the soil, dissolved oxygen, and soil erodibility. The probability of detecting PCE decreased as both sand content of the soil and soil erodibility increased. Sand content of soil has been identified as being a possible surrogate for another soil property, such as unsaturated zone hydraulic conductivity.

Soil erodibility also likely is a surrogate variable. Soil erodibility is defined as the susceptibility of a soil to detachment and transport by water (Natural Resources Conservation Service, 2005). Some of the most important properties that affect soil erodibility are texture, organic matter content, structure size and class, and saturated hydraulic conductivity of the soil (Natural Resources Conservation Service, 2005). Soil erodibility factors are measured by applying a series of simulated rainstorms on freshly tilled plots and computed using soil characteristics such as size fraction, organic matter content, and permeability. Thus, soil erodibility is a surrogate variable that represents the interaction between several soil properties. The particular combination of soil properties that the soil erodibility term represents is strongly inversely related to the probability of detecting PCE in ground water, and thus, soil erodibility may represent a property such as saturated vertical hydraulic conductivity of the soil zone, which would be expected to strongly influence the occurrence of solvents in ground water.

The probability of detecting PCE also increased as dissolved-oxygen content of ground water increased (table 19). PCE is known to biodegrade through reductive dechlorination (Swindoll and Troy, 1996). In oxic ground water, less biotransformation of PCE occurs by reductive dechlorination, and

therefore, a higher concentration remains in solution. Thus, the probability of detecting PCE should be greater in oxic ground water compared to anoxic ground water.

The probability of detecting PCE in ground water also was weakly associated with the number of Resource Conservation and Recovery Act (RCRA) sites within 1 km of the wells, the depth to the top of the screened interval in the wells, and the numbers of septic systems within 1 km of the wells (table 19). RCRA sites are facilities that generate, transport, store, or dispose of hazardous waste, as defined under RCRA, and are required to register the amounts and types of waste with the USEPA (U.S. Environmental Protection Agency, 2004c). RCRA sites may be sources of solvents to ground water if solvents were released at the site.

The probability of detecting TCA in ground water was strongly associated with dissolved oxygen, urban land use, population density, depth to the top of the screened interval, and recharge (table 19). Except for depth to the top of the screened interval, the probability of detecting TCA in ground water increased as each of these variables increased. The probability of detecting TCA in ground water decreased as depth to the top of the screened interval increased.

Population density and urban land use are aggregate surrogate variables for sources of TCA to ground water. Dissolved oxygen controls the fate of TCA in ground water. TCA has been shown to biodegrade under anoxic conditions, and thus, the probability of detecting TCA should be greater in oxic ground water compared to anoxic ground water (Parsons and others, 1985; Semprini and others, 1992). Recharge is the transport mechanism that moves solvents from the surface or near-surface areas through the vadose zone to ground water. As recharge increases, the probability of detecting a contaminant transported through the vadose zone also should increase. The probability of detecting TCA in ground water was weakly associated with the number of CERCLA sites within 1 km of the wells and the numbers of septic systems within 1 km of the wells (table 19).

The probability of detecting TCE in ground water was strongly associated with population density (table 19). The probability of detecting TCE increased as population density increased. Population density is an aggregate surrogate variable for sources of TCE to ground water. The probability of detecting TCE in ground water was weakly associated with dissolved oxygen, the number of RCRA sites within 1 km of the wells, the number of CERCLA sites within 1 km of the wells, and the average diameter of the well casing (table 19).

The probability of detecting TCE in ground water increased as the average diameter of the well increased. The average diameter of the well casing is a surrogate for average discharge from the well. Larger diameter wells generally have larger pumping capacities. An examination of NAWQA data indicated a good correlation between average discharge from a well and average casing diameter (Spearman's rho 0.398; $p = 0$). Wells with higher pumping rates usually obtain water from larger volumes of an aquifer compared to wells with smaller pumping rates. Larger volumes of aquifer contribution to a well

generally are obtained from a larger geographical area that can provide a greater number of potential sources of TCE to ground water.

Summary of Significantly Associated Explanatory Variables

Table 20 is a summary of explanatory variables that were significantly associated with the probability of occurrence of any individual solvent. Included in this table is the explanatory variable, the rank sum of the variable, the number of individual solvents that were associated with the variable, and the type of variable—source, transport, or fate. The rank sum was computed by ranking each variable associated with each individual solvent according to the standardized coefficient, with higher standardized coefficients given lower ranks. Ties were given the same rank. The ranks for each explanatory variable were then summed across each solvent for a rank sum. The lower rank sums indicate a variable that was consistently more strongly associated with solvent occurrence.

Table 21 lists the ranking of each type of variable that was associated with the probability of occurrence of individual solvents. The ranking was obtained by summing the number of times each variable type was significantly associated with each solvent. These numbers were then normalized relative to the total number of variable types available in the logistic regres-

sion analyses and then ranked for each solvent. Lower ranks indicate a variable type that was more strongly and frequently associated with solvent occurrences.

Dissolved-oxygen content, percent urban land use around the well, and population density were the variables most strongly and frequently associated with the probability of occurrence of solvents in ground water (table 20). These variables represent the sources and fate of solvents.

Dissolved oxygen was the only variable associated with the probability of occurrence of one or more solvents or individual solvents that could be attributed to the fate of solvents in ground water. Dissolved oxygen was associated with the probability of occurrence of one or more solvents and three individual solvents, and fate was the most important type of explanatory variable for every individual solvent except methylene chloride (table 21). In every case where dissolved oxygen was related to the probability of occurrence of solvents, the probability of occurrence increased with increasing dissolved-oxygen content (table 19). This indicates that increased rates of degradation of solvents are occurring in conditions of low dissolved oxygen. Reductive transformation reactions are the most important for solvents in ground water (Beek, 2001). Thus, it is presumed that solvents are preferentially degraded in conditions of relatively low dissolved oxygen in ground water and consequently are detected more frequently when dissolved-oxygen concentrations are relatively high.

Table 20. Rank sum and number of solvents associated with each hydrogeologic and anthropogenic variable in ground water.

[km, kilometer; RCRA, Resource Conservation and Recovery Act; CERCLA, Comprehensive Environmental Response, Compensation, and Liability Act]

Explanatory variable	Rank sum	Number of solvents associated with variable	Type of variable	Association strength
Dissolved oxygen	12	3	Fate	
Urban land use	13	3	Source	Strong
Population density	13	3	Source	
Sand content of soil	19	2	Transport	
Depth to top of screened interval	22	2	Transport	Moderate
RCRA sites within 1 km	22	2	Source	
CERCLA sites within 1 km	24	2	Source	
Soil bulk density	24	1	Transport	
Soil erodibility	24	1	Transport	
Recharge	25	1	Transport	Weak
Septic systems within 1 km	26	2	Source	
Casing diameter	27	1	Transport	
Median year of home construction	27	1	Source	

Table 21.   Ranking of type of variable associated with each solvent in ground water based on significant associations.

[PCE, perchloroethene; TCA, 1,1,1-trichoroethane; TCE, trichoroethene]

Variable type	Ranking of significant associations			
	Methylene chloride	PCE	TCA	TCE
Source	1	2	2	2
Transport	1	2	3	3
Fate	3	1	1	1

Urban land use and population density represent sources of solvents to ground water. At least one of these two variables was associated with the probability of occurrence of one or more solvents and every individual solvent. In every case where either or both of these two variables were related to the probability of occurrence of solvents, the probability of occurrence increased with increasing percent urban land use or population density (table 19). Unlike specific sources of solvents to ground water, these variables represent aggregate surrogate variables for input of solvents to ground water because one or more events or actions likely have resulted in release of solvents to the environment in these areas. For example, urban land use may represent releases of solvents from activities such as leaking USTs, spills at bulk loading and unloading facilities, and runoff from commercial/industrial areas where solvents have been deposited from air. Population density and year of home construction also probably are aggregate surrogate variables for solvent input to ground water just like urban land use. Population density was strongly correlated with urban land use (Spearman's rho 0.73; $p = 0$), and year of home construction also was strongly correlated with urban land use (Spearman's rho 0.131; $p = 0$).

The variables that were moderately associated with the probability of occurrence of solvents, in magnitude and frequency, included sand content of the soil, depth to the top of the screened interval, and the number of CERCLA and RCRA sites within 1 km of the wells (table 20). These variables represent sources and transport of solvents to ground water. Transport and sources variables were less important than fate in determining the probability of occurrence for every individual solvent except methylene chloride (table 21).

Sand content of the soil and depth to the top of the screened interval are properties that indirectly affect the transport of solvents to ground water. In every case where soil sand content was associated with the probability of occurrence of solvents, the probability of occurrence decreased with increasing soil sand content (table 19). Although these results might seem to be the opposite of what is expected, the consistency in the results indicates that the association is valid. Soil sand content is believed to be a surrogate for the unsaturated hydraulic conductivity of the soil zone. As mentioned, in the vadose zone at low pressure head or water content, the unsaturated hydraulic

conductivity of a fine-textured soil may be greater than that of a coarse soil (Stephens, 1996). Thus, in some cases, the hydraulic conductivity of soil in the vadose zone may vary inversely with soil sand content.

Depth to the top of the screened interval is believed to be roughly equivalent to the depth to the top of the aquifer and represents the distance needed for solvents to move from the land surface, or from their point of release in the vadose zone, through the vadose zone to ground water. In every case where depth to the top of the screened interval was related to the probability of occurrence of solvents, the probability of occurrence decreased with increasing depth (table 19). As distance to the aquifer from the release point increases, the time required for a solvent to reach it also increases provided there is no short cutting of traveltime to the aquifer. This increased time allows for increased attenuation of solvent concentrations through natural loss processes such as biodegradation, sorption, dispersion, and volatilization.

The numbers of CERCLA and RCRA sites within 1 km of the wells represent sources of solvents to ground water. In every case where either or both of these variables were related to the probability of occurrence of solvents, the probability of occurrence increased with increasing number of sites near the wells (table 19). Unlike urban land use and population density, these terms may represent specific sources of solvents to ground water or they could be surrogates for indirect sources. The legislation that established CERCLA and RCRA sites was designed to protect ground water at hazardous waste sites and to clean up uncontrolled hazardous waste sites (U.S. Environmental Protection Agency, 2005a). Since the enactment of the legislation that established these sites more than 20 years ago, data from thousands of hazardous waste sites have been gathered and analyzed. CERCLA sites that are rated as highest priority for cleanup are included on the National Priority List and also are called Superfund sites.

An early survey of 183 hazardous waste sites in the United States indicated that four of the top five most frequently identified organic contaminants were solvents (methylene chloride, TCE, PCE, and 1,2-dichloroethane) (Pankow and Cherry, 1996). The USEPA indicates that PCE, TCE, and methylene chloride are among the chemicals most commonly found at Superfund sites (U.S. Environmental Protection Agency, 2005a). Thus, these sites would be plausible sources of solvents to ground water. However, it is not known if the solvents detected in ground water in this report specifically had a source at these sites.

The remaining associated variables, with one exception, represent the source or transport of solvents and were only weakly and infrequently associated with the probability of occurrence of solvents in ground water (table 20). The one exception was the number of septic systems within 1 km of the wells. Although only weakly associated, this variable was significant in regressions for PCE, TCA, and one or more solvents (table 19). In every case where the number of septic systems was related to the probability of occurrence of solvents, the probability of occurrence increased with increasing number

of septic systems near the wells (table 19). Septic systems likely represent direct sources of solvents to ground water.

There are many lines of evidence that septic systems can be sources of solvents to ground water. Many types of household products contain solvents, and it is likely that these are disposed of in septic systems. At one time, fluids used to clean septic tanks were known to contain TCE and methylene chloride. In fact, in 1976 New York State revealed that aquifers on Long Island were extensively contaminated by TCE because of homeowner use of septic tank cleaning products containing TCE (Pankow and Cherry, 1996).

DeWalle and others (1980) found five VOCs, two of which were solvents examined in this report (methylene chloride and PCE), in samples of septic tank effluent from a community septic tank serving 91 homes in a subdivision of Tacoma, Washington. Viraraghavan and Hashem (1986) found methylene chloride, along with two other VOCs, in septage and septic tank effluent from a house in Regina, Canada. Ayres Associates (1993) found methylene chloride and TCA in septage and septic tank effluent beneath the septic system leach fields of homes in several Florida counties.

Septic systems consist of two reactor areas: (1) the septic tank that acts as an anaerobic reactor, and (2) the drainage field or leach field that acts as an aerobic reactor. Wastewater from the house first flows into a holding tank called the septic tank. The main purpose of the septic tank is to settle solid particles and separate grease from the wastewater. In addition to these purposes, the septic tank also acts as an anaerobic reactor and begins breakdown of organic material. If solvents from domestic products are disposed of in the septic system, some reductive biotransformation of them may occur in the septic tank.

Effluent from the septic tank then flows through a series of trenches in the soil filled with gravel, called the leach field. In this area, further breakdown of organic material occurs by aerobic biodegradation. Because solvents primarily biotransform in low dissolved-oxygen conditions, little breakdown of solvents will occur once they have been passed through the septic tank to the leach field.

Although solvents may be transformed in the septic tank, the residence time of dissolved-organic material in the septic tank is relatively short. Because of this relatively short residence time, much of the mass of solvents disposed of in septic systems may not be removed. In addition, quick transfer of material from the septic tank to the leach field can occur if the septic system is improperly designed, installed, or maintained. For example, septic tanks require pumping every 3 to 5 years to remove solids from the tank. If this is not done, a septic tank can fill with solids, and wastewater from the home can be transferred more quickly to the leach field. This "short-circuiting" of fluid through the septic tank could allow solvents from domestic products to enter the vadose zone with virtually no breakdown.

Most of the remaining variables that were weakly associated with the probability of occurrence of solvents were transport variables (table 20). Transport of solvents generally involves recharge, permeability, and distance. Recharge, precipitation moving from the land surface to the water table, transports solvents to ground water through advection. Permeability facilitates, or impedes, the vertical movement of water from the surface to ground water and the movement of ground water through an aquifer. Distance affects the amount of time required for a solvent to reach ground water.

Soil bulk density, soil erodibility, recharge, and casing diameter, were weakly and infrequently associated with the probability of occurrence of solvents in ground water (table 20). Soil bulk density and soil erodibility are believed to be surrogates for the unsaturated and saturated hydraulic conductivities of the soil zone. These properties represent the ability and speed through which solvents could move through the soil zone to ground water, although the specific relations between these factors and hydraulic conductivity are not known. Although transport processes would seem to be most important for unconfined or semi-confined aquifers, aquifer confinement was not found to be significantly related to the occurrence of solvents. Transport appears to be important to the probability of occurrence of solvents regardless of the confining conditions of the aquifer.

Casing diameter was weakly associated with the probability of occurrence of TCE. Casing diameter is believed to be a surrogate for discharge from the well. As discharge from the well increases, the well draws from a larger volume of water in the aquifer. Drawing from a larger volume of ground water increases the chances for including ground water that is contaminated by solvents. In addition, drawing from a larger volume of ground water also means drawing from a larger area of recharge to the aquifer, which increases the chances for intercepting releases of solvents by increasing the zone of influence of the well and also increasing the chances for short circuiting transport of solvents through higher permeable zones. These mechanisms could result in an increase in the probability of detecting solvents with an increase in casing diameter. However, increased discharge from a well could have the opposite effect of decreasing the likelihood of detecting a solvent due to dilution effects (Einarson and Mackay, 2001).

Recharge is believed to be the primary mechanism for moving solvents from their point of release to ground water, although diffusion of gas-phase concentrations of some VOCs from the atmosphere to shallow ground water can occur after long periods of time (Pankow and others, 1997). Recharge was only associated with the probability of occurrence of TCA. The reason for the lack of associations of the recharge with other solvents is unclear, but large releases of a solvent from a concentrated source like a UST can move directly through the vadose zone to ground water by gravity. Once in contact with ground water, the density of the solvent can cause it to continue to sink through ground water until it reaches the base of the aquifer. In this situation, the solvent becomes a continual source of contamination to ground water without requiring transport by recharge. This process is illustrated in figure 30. It is possible that many concentrated discharges of solvents behave in this manner thereby reducing the relation of solvents to recharge or even to their sources.
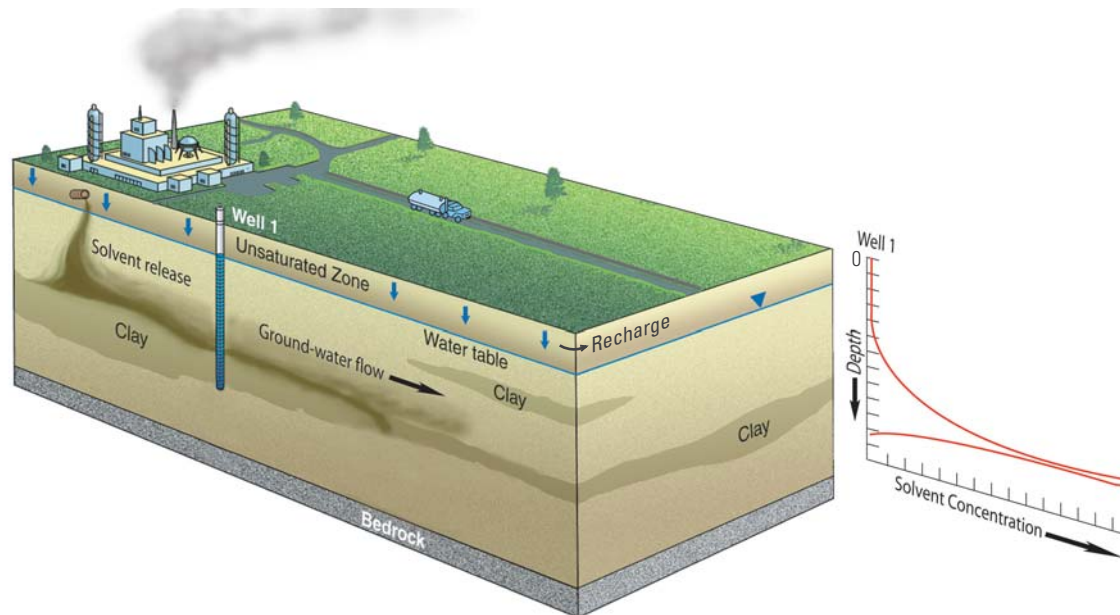
Figure 30.   Movement of solvents through an aquifer from a concentrated discharge release.

For TCA and TCE, transport was the least important type of variable associated with solvent occurrence (table 21). In the case of PCE, source and transport variables were both moderately important to solvent occurrence. For methylene chloride, source and transport variables were the most important variable types although they were mostly only weakly associated.

Implications

All of the four solvents, with the exception of methylene chloride, were in the top 10 most frequently detected VOCs in ground water, source water, and drinking water, and between 40 and 47 VOCs analyzed were detected at an assessment level of 0.2 µg/L. Thus, out of a large number of VOCs detected, solvents were some of the most frequently occurring in ground water, source water, and drinking water. Determining the occurrence of solvents in ground-water resources is important, especially for ground-water resources that are used as drinking-water supplies. Also, the frequent detection of solvents in ground water suggests that analyzing for a full suite of solvents in ground water is important in obtaining a complete picture of environmental occurrence.

In ground water, the detection frequencies of individual solvents were higher at an assessment level of 0.02 µg/L than at an assessment level of 0.2 µg/L. Thus, low concentrations of solvents occur more frequently in ground water than high concentrations. Use of analytical methods with low-level detection limits for solvents are necessary to fully ascertain the

environmental distribution of solvents. Low-level analyses may not be important for concentrations of solvents relative to MCLs. However, low-level analyses could be important for determining the sources of solvents, as a potential early warning regarding the vulnerability of an aquifer, and for determining trends and patterns in occurrence of solvents in aquifers.

The rankings of detection frequencies of individual solvents were identical in ground water and source water nationwide at an assessment level of 0.2 µg/L and were as follows, from highest to lowest: PCE, TCE, TCA, and methylene chloride. The similarity of the rankings is probably indicative of similarities in the number and strength of sources of each solvent and the transport and fate mechanisms affecting each between ground water and source water.

Mixtures were a common mode of occurrence for solvents, with mixtures occurring in about 30 to 40 percent of ground-water and source-water samples with detections of one or more solvents at an assessment level of 0.2 µg/L. For both ground water and source water, the mixture of PCE-TCE was the most frequently occurring. The frequent occurrence of this mixture probably is the result of the transformation of PCE to TCE through reductive dechlorination (fig. 1).

Because reductive dechlorination occurs anaerobically, the occurrence of PCE should be higher in ground water with relatively high dissolved oxygen compared to ground water with relatively low dissolved oxygen. In ground-water samples, the occurrence of PCE was 12.6 percent in oxic ground water and 6.3 percent in anoxic ground water. In this case, oxic ground water was defined as having dissolved oxygen greater

than or equal to 0.5 mg/L, and anoxic ground water was defined as having dissolved oxygen less than 0.5 mg/L. In addition, the molar concentration ratios of PCE/TCE were three times higher in oxic ground water than in anoxic ground water. These lines of evidence support the hypothesis that PCE is being degraded to TCE in anoxic ground water.

Evaluation of mixtures of solvents in ground-water resources is important, especially for ground water used for drinking-water supplies. The study of chemical mixtures and their effect on human health is an important area of research because of potential human-health effects of mixtures (Suk and others, 2002). For example, exposure to mixtures of TCE, PCE, and TCA have been shown, through computer modeling, to increase the blood concentration of TCE in humans, and this could lead to increased potential health effects from TCE exposure, such as an increased chance for renal tumors (Dobrev and others, 2002).

In ground water, TCE and PCE ranked in the upper one-half of the total number of detected VOCs in terms of the median quantified concentrations at an assessment level of 0.02 µg/L. In source water, all four solvents ranked in the upper one-half of the total number of detected VOCs in terms of the median quantified concentrations at an assessment level of 0.2 µg/L. In drinking water, TCE and PCE ranked in the upper one-half of the total number of detected VOCs in terms of the median quantified concentrations at an assessment level of 0.2 µg/L. Thus, in general, the four solvents had higher median quantified concentrations relative to other VOCs in ground water, source water, and drinking water.

Relative to the total number of VOCs with MCLs, solvents ranked consistently high in terms of the frequency of concentrations greater than MCLs. In fact, PCE and TCE ranked 1 and 2 for both source water and drinking water. In ground water, PCE ranked 1 and TCE ranked 3. Therefore, solvents have a higher frequency of concentrations greater than the MCL relative to other VOCs in ground water, source water, and drinking water. Because of this, solvents appear to be the VOCs that pose the greatest threat to human health in ground water and drinking water. The concentrations of solvents in aquifers need to be understood, especially in aquifers used to supply drinking water. In addition, it may be necessary to control the sources of solvents to domestic and public wells in order to be protective of human health.

When confined to data from 12 Northeast and Mid-Atlantic States, the detection frequencies of one or more solvents and individual solvents (with the exception of methylene chloride) were similar between ground water, source water, and drinking water. When examined at a national scale, the detection frequencies of one or more solvents and individual solvents were similar between ground water and source water, although they were lower than the detection frequencies computed for the 12 Northeast and Mid-Atlantic States. Thus, the occurrence of solvents is relatively uniform with respect to the intended end use of ground water. However, the occurrence of solvents may not be uniform with respect to human activity in the area above ground water.

One likely reason for the higher detection frequencies of solvents in the Northeast and Mid-Atlantic regions of the country is that these are areas of higher human population and greater human activities compared to the country as a whole. Areas with greater population and human activity have more potential sources of solvents and a greater number of concentrated discharges to the environment. Sampling and monitoring of solvents in ground water above areas of increased levels of human activity (for example, areas of higher population density) is important.

In general, the detection frequencies of individual solvents were higher in ground water beneath urban land-use areas compared to ground water in aquifer studies (mixed land-use areas) or beneath agricultural land-use areas. The exception to this was the occurrence of methylene chloride that showed no relation to any type of land use. Urban areas have a greater number of sources of solvents to ground water and have more concentrated solvent discharges compared to rural areas. The ranking of detection frequencies of individual solvents in ground water beneath urban land-use areas was as follows: PCE, TCE, TCA, and methylene chloride. Again, the rankings probably are indicative of the number and strength of sources of each solvent and the transport and fate mechanisms affecting each. The lack of a relation between the occurrence of methylene chloride in ground water and land use suggests a different source for this solvent relative to the others. Some concentrations of methylene chloride may be the result of biodegradation of other VOCs like trichloromethane (chloroform) (Matheson and Tratnyek, 1994). Sampling of aquifers in areas of variable land use is important to most accurately represent water quality with respect to solvents.

The concentrations of PCE, TCE, and TCA were higher in ground water than in drinking water. The reason for higher overall concentrations of these solvents in ground water is not clear. However, the differences in the frequencies of concentrations greater than the MCLs for PCE and TCE were not statistically significant in any comparison between ground water, source water, and drinking water. Therefore, the distribution of concentrations of solvents greater than the MCL was not different with respect to the intended use of ground water.

The probability of occurrence of solvents in ground water was associated with a variety of source, transport, and fate variables. Concentrated releases of solvents, like those from regulated hazardous waste facilities, were associated with the occurrence of solvents in ground water. However, the strongest sources associated with the occurrence of solvents were urban land use and population density. These variables represent aggregate surrogate terms for overall human input of solvents to the environment.

It might be expected that a concentrated source of solvents like USTs at dry-cleaning facilities would be related to the probability of occurrence of solvents in ground water. But the number of USTs identified as linked with a dry-cleaning operation was very small. Only 68 samples (1.3 percent) had one or more dry-cleaning USTs in proximity, and only 32 samples (0.6 percent) had one or more leaking dry-cleaning USTs in

proximity. The numbers of samples with dry-cleaning USTs in proximity were too small to establish an association.

One explanation for the weak or non-existent association between the occurrence of solvents and concentrated sources like regulated hazardous waste facilities or dry-cleaning operations is that dispersed sources are more important in contributing solvents to ground water. Many potential sources of solvents exist, as described previously in this report, and most of these sources are dispersed. Thus, variables like population density and urban land use better represent these more dispersed and low-concentration sources of solvents.

Another possible explanation for the weaker association of solvents with concentrated sources compared to dispersed sources is the unique behavior of solvents in ground water. As mentioned, releases of pure solvent from a concentrated source like a UST can move directly through the saturated zone due to the density of these compounds relative to water. Once an impermeable layer is reached, the pure solvent could then move downslope with respect to gravity and migrate some distance from the original release site (fig. 30). Although the solvent had a concentrated source, movement of the pure phase along the impermeable layer has displaced it from the source. In addition, lateral spreading of solvents in the saturated zone due to geologic heterogeneities also can cause an offset in the location of the solvent from its original source (Pankow and Cherry, 1996). Thus, concentrations of a solvent from a point release could be detected at a substantial distance from the release site and show no apparent association to it.

More research is needed into the specific sources of solvents to ground water. If concentrated sources like regulated hazardous waste facilities or dry-cleaning operations are found to be the main source of solvents to ground water, then it will be important to attempt to control these sources through siting regulations and UST protection. If dispersed sources like urban land use are found to be the main source of solvents to ground water, then it will be important to attempt to control these sources through stormwater management and treatment and best management practices.

Transport variables that were found to be most strongly associated with the occurrence of solvents were soil properties related to the hydraulic conductivity of the soil zone. Depth to the top of the aquifer and recharge were important for TCA. Aquifers with overlying soil zones that have high hydraulic conductivity may be more susceptible to contamination by solvents. Thus, it is important to understand the susceptibility of aquifers by fully ascertaining the hydraulic properties of the vadose zone.

The variable associated with fate of solvents in ground water was dissolved-oxygen content, with solvents being more persistent in relatively high dissolved-oxygen conditions compared to relatively low dissolved-oxygen conditions. This variable was strongly associated with one or more solvents and with PCE and TCA. Reductive dechlorination of PCE may be an important factor in controlling the occurrence of this solvent, and its daughter product TCE, in ground water. Understanding of the redox conditions of aquifers is important in fully evaluating solvent occurrence.

Summary

The U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program collected or compiled data on solvents in water during 1993–2002. The data came from three sources: (1) the NAWQA Program that sampled ground water throughout the United States or compiled similar data, (2) a collaborative effort of the NAWQA Program and other organizations that sampled ground water used as a source of drinking water throughout the United States, and (3) the NAWQA Program that compiled data on drinking water from ground water for community water systems (CWSs) in 12 Northeast and Mid-Atlantic States. Occurrence, distribution, and concentrations of solvents were examined for four commonly used solvents—methylene chloride, perchloroethene (PCE), 1,1,1-trichloroethane (TCA), and trichloroethene (TCE).

Out of 51 to 55 volatile organic compounds (VOCs) analyzed in samples, solvents were some of most frequently detected VOCs in all data sets. Although low concentrations of VOCs commonly were detected in ground water, PCE and TCE had higher median detected concentrations than other VOCs. Relative to other VOCs, solvents also were ranked high in terms of the frequency of concentrations greater than the Maximum Contaminant Level in all data sets. Mixtures were a common mode of occurrence of solvents. In samples of ground water or source water where at least one solvent was detected, multiple solvents occurred in 30 to 40 percent. When confined to 12 Northeast and Mid-Atlantic States, the detection frequencies of solvents were similar among data sets. In general, the detection frequencies of solvents were higher in ground water underlying urban land-use areas compared to ground water underlying mixed or agricultural land-use areas.

The probability of occurrence of solvents in ground water was most strongly associated with dissolved-oxygen content. This variable represents processes that control the fate of solvents in ground water with solvents being more persistent in relatively high dissolved-oxygen conditions compared to relatively low dissolved-oxygen conditions.

The probability of occurrence of solvents in ground water also was strongly and frequently associated with urban land use and population density. Although these dispersed sources were more strongly associated with solvent occurrence in ground water than were concentrated sources like regulated hazardous waste sites, concentrated sources like hazardous waste sites could contribute a substantial mass of solvents to ground water in proximity to these facilities. The probability of occurrence of solvents in ground water also was strongly associated with decreasing sand content of the soil and the depth to the top of the screened interval. These variables represent properties that affect the transport of solvents through the soil zone to ground water.

It is important for ground-water resource managers to understand the contamination potential posed by solvents, especially in resources that are critical as drinking-water supplies.

Low-level analytical methods are most useful for determining the complete environmental distribution of solvents in ground water. Low-level analyses could be important for determining the sources of solvents, as a potential early warning on the vulnerability of an aquifer, and for determining trends and patterns in occurrence of solvents in aquifers. Evaluation of mixtures is important in determining the health implications of solvents in ground water, especially ground water used for drinking-water supplies. To protect ground-water resources, it is important for ground-water managers to (1) delineate the redox conditions of ground water in the aquifer in order to understand the fate of solvents, (2) determine and control the sources, or potential sources, of solvents to ground water, and (3) establish the susceptibility of aquifers by fully ascertaining the hydraulic properties of the saturated zone and vadose zone.

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Appendixes

Appendix 1.   VOCs and their U.S. Environmental Protection Agency Maximum Contaminant Levels (U.S. Environmental Protection Agency, 2004a).

[Four solvents examined in this report are bolded. VOC, volatile organic compound; MCL, Maximum Contaminant Level; μg/L, microgram per liter]

VOC	MCL (μg/L)	VOC	MCL (μg/L)
Tetrachloromethane	5	1,2-Dichloropropane	5
1,2-Dichloroethane	5	*trans*-1,2-Dichloroethene	100
Methylbenzene	1,000	1,2,4-Trichlorobenzene	70
Benzene	5	1,4-Dichlorobenzene	75
Chlorobenzene	100	Chloroethene	2
Ethylbenzene	700	**Trichloroethene (TCE)**	5
Methylene chloride	5	*cis*-1,2-Dichloroethene	70
Perchloroethene (PCE)	5	Styrene	100
1,1-Dichloroethene	7	1,2-Dibromoethane	.05
1,1,1-Trichloroethane (TCA)	200	Xylenes (mixed isomers)	10,000
1,1,2-Trichloroethane	5	1,2-Dibromo-3-chloropropane	.2
1,2-Dichlorobenzene	600	Total trihalomethanes	80

Appendix 2.   Ranking of 55 VOCs relative to detection frequency in ground water at an assessment level of 0.2 µg/L.

[Four solvents examined in this report are bolded]

VOC	Rank	VOC	Rank
Chloroform	1	Vinyl chloride	29
Methyl *tert*-butyl ether	2	Isopropylbenzene	30
Perchloroethene (PCE)	**3**	Chloroethane	31
Trichloroethene (TCE)	**4**	*tert*-Amyl methyl ether	32
1,1,1-Trichloroethane (TCA)	**5**	*o*-Xylene	33
Toluene	6	*n*-Propylbenzene	34
Dichlorodifluoromethane	7	Chlorobenzene	35
Xylenes (mixed isomers)	8	*n*-Butylbenzene	36
Bromodichloromethane	9	1,4-Dichlorobenzene	37
1,1-Dichloroethane	10	Trichlorotrifluoroethane	38
Trichlorofluoromethane	11	1,2-Dichlorobenzene	39
Chloromethane	12	Diisopropyl ether	40
Methylene chloride	**13**	Ethylene dibromide	41
1,2,4-Trimethylbenzene	14	Bromomethane	42
1,2-Dichloropropane	15	Styrene	43
Benzene	16	1,1,2-Trichloroethane	[1]44
cis-1,2-Dichloroethene	17	1,2,3-Trichlorobenzene	[1]44
Bromoform	18	1,2,4-Trichlorobenzene	[1]44
trans-1,2-Dichloroethene	19	1,3-Dichlorobenzene	[1]44
Dibromochloromethane	20	Acrolein	[1]44
1,1-Dichloroethene	21	Acrylonitrile	[1]44
1,2,3-Trichloropropane	22	Ethyl *tert*-butyl ether	[1]44
Naphthalene	23	Hexachlorobutadiene	[1]44
1,2-Dichloroethane	24	Hexachloroethane	[1]44
Dibromochloropropane	25	Vinyl bromide	[1]44
m- & *p*-Xylene	26	*cis*-1,3-Dichloropropene	[1]44
Ethylbenzene	27	*trans*-1,3-Dichloropropene	[1]44
Carbon tetrachloride	28		

[1]Compound not detected in any of the samples.

Appendix 3. Ranking of 52 VOCs relative to detection frequency in source water at an assessment level of 0.2 µg/L.

[Four solvents examined in this report are bolded]

VOC	Rank	VOC	Rank
Chloroform	1	Isopropylbenzene	27
Dibromochloromethane	2	**Methylene chloride**	**28**
Bromodichloromethane	3	1,2-Dichloropropane	29
Methyl *tert*-butyl ether	4	1,2,3-Trichloropropane	30
Bromoform	5	1,2-Dichlorobenzene	30
Perchloroethene (PCE)	**6**	1,4-Dichlorobenzene	30
Trichloroethene (TCE)	**7**	Bromomethane	30
1,1-Dichloroethane	8	Chlorobenzene	30
cis-1,2-Dichloroethene	8	Chloroethane	30
1,1,1-Trichloroethane (TCA)	**10**	Ethyl *tert*-butyl ether	30
1,1-Dichloroethene	11	Naphthalene	30
Carbon tetrachloride	12	Trichlorotrifluoroethane	30
Trichlorofluoromethane	12	Vinyl chloride	30
m- & *p*-Xylene	14	*n*-Butylbenzene	[1]30
o-Xylene	15	1,1,2-Trichloroethane	[1]41
Dichlorodifluoromethane	16	1,2,3-Trichlorobenzene	[1]41
Toluene	17	1,2,4-Trichlorobenzene	[1]41
Ethylbenzene	18	1,3-Dichlorobenzene	[1]41
1,2-Dichloroethane	19	Acrylonitrile	[1]41
Chloromethane	19	Hexachlorobutadiene	[1]41
Styrene	21	Hexachloroethane	[1]41
Benzene	22	Vinyl bromide	[1]41
Diisopropyl ether	23	*cis*-1,3-Dichloropropene	[1]41
Ethylene dibromide	23	*n*-Propylbenzene	[1]41
tert-Amyl methyl ether	23	*trans*-1,2-Dichloroethene	[1]41
1,2,4-Trimethylbenzene	26	*trans*-1,3-Dichloropropene	[1]41

[1]Compound not detected in any of the samples.

Appendix 4.   Ranking of 51 VOCs relative to detection frequency in drinking water at an assessment level of 0.2 µg/L.

[Four solvents examined in this report are bolded]

VOC	Rank	VOC	Rank
Chloroform	1	Trichlorofluoromethane	27
Bromodichloromethane	2	1,2-Dichlorobenzene	28
Dibromochloromethane	3	Chloroethane	29
Bromoform	4	Bromomethane	30
Methyl *tert*-butyl ether	5	1,2,4-Trimethylbenzene	31
1,1,1-Trichloroethane (TCA)	**6**	*n*-Butylbenzene	32
Perchloroethene (PCE)	**7**	Vinyl chloride	33
Trichloroethene (TCE)	**8**	*n*-Propylbenzene	34
Toluene	9	1,2,4-Trichlorobenzene	35
Xylenes (mixed isomers)	10	Ethylene dibromide	36
Methylene chloride	**11**	1,1,2-Trichloroethane	37
Ethylbenzene	12	Chlorobenzene	38
1,2-Dichloroethane	13	Styrene	39
1,1-Dichloroethane	14	1,2,3-Trichloropropane	40
o-Xylene	15	*cis*-1,3-Dichloropropene	41
cis-1,2-Dichloroethene	16	Hexachlorobutadiene	42
1,1-Dichloroethene	17	Dibromochloropropane	43
Chloromethane	18	Isopropylbenzene	44
Benzene	19	1,2,3-Trichlorobenzene	[1]45
Dichlorodifluoromethane	20	1,3-Dichlorobenzene	[1]45
Carbon tetrachloride	21	Acrolein	[1]45
1,4-Dichlorobenzene	22	Acrylonitrile	[1]45
m- & *p*-Xylene	23	Hexachloroethane	[1]45
1,2-Dichloropropane	24	Trichlorotrifluoroethane	[1]45
Naphthalene	25	*trans*-1,3-Dichloropropene	[1]45
trans-1,2-Dichloroethene	26		

[1]Compound not detected in any of the samples.

Appendix 5.   Ranking of median concentration of 47 VOCs that had quantifiable concentrations in ground water, at an assessment level of 0.02 µg/L.

[Four solvents examined in this report are bolded]

VOC	Rank	VOC	Rank
Naphthalene	1	Dibromochloromethane	25
Dibromochloropropane	2	Chlorobenzene	26
1,2-Dichloroethane	3	**1,1,1-Trichloroethane (TCA)**	**27**
1,2,3-Trichloropropane	4	1,4-Dichlorobenzene	28
Vinyl chloride	5	*o*-Xylene	29
n-Butylbenzene	6	**Methylene chloride**	**30**
Bromoform	7	Toluene	31
Methyl *tert*-butyl ether	8	Benzene	32
Dichlorodifluoromethane	9	Chloroethane	32
1,2-Dichloropropane	10	Styrene	34
tert-Amyl methyl ether	11	1,3-Dichlorobenzene	35
Trichloroethene (TCE)	**12**	*n*-Propylbenzene	36
Diisopropyl ether	13	1,2,4-Trimethylbenzene	37
Trichlorotrifluoroethane	14	1,1-Dichloroethene	38
1,2-Dichlorobenzene	15	Ethylbenzene	39
Trichlorofluoromethane	16	Chloromethane	40
Isopropylbenzene	17	1,1,2-Trichloroethane	41
Chloroform	18	*m*- & *p*-Xylene	42
cis-1,2-Dichloroethene	19	Hexachlorobutadiene	43
Bromomethane	20	*trans*-1,2-Dichloroethene	44
Perchloroethene (PCE)	**20**	Ethyl *tert*-butyl ether	45
Carbon tetrachloride	22	1,2,3-Trichlorobenzene	46
Bromodichloromethane	23	1,2,4-Trichlorobenzene	46
1,1-Dichloroethane	24		

Appendix 6. Ranking of frequency of exceedance of Maximum Contaminant Levels for VOCs that had quantifiable concentrations in ground water.

[Four solvents examined in this report are bolded]

VOC	Rank	VOC	Rank
Perchloroethene (PCE)	**1**	1,1,2-Trichloroethane	[1]12
Dibromochloropropane	2	1,2,4-Trichlorobenzene	[1]12
Trichloroethene (TCE)	**3**	1,2-Dichlorobenzene	[1]12
Benzene	4	1,4-Dichlorobenzene	[1]12
1,2-Dichloropropane	5	Carbon tetrachloride	[1]12
Ethylene dibromide	6	Chlorobenzene	[1]12
1,1-Dichloroethene	7	Ethylbenzene	[1]12
Vinyl chloride	8	Styrene	[1]12
Methylene chloride	**9**	Toluene	[1]12
cis-1,2-Dichloroethene	10	*trans*-1,2-Dichloroethene	[1]12
1,2-Dichloroethane	11	Trihalomethanes	[1]12
1,1,1-Trichloroethane (TCA)	[1]**12**	Xylenes	[1]12

[1]Frequency of exceedance was zero.

Appendix 7. Ranking of median concentration of 40 VOCs that had quantifiable concentrations in source water, at an assessment level of 0.2 µg/L.

[Four solvents examined in this report are bolded]

VOC	Rank	VOC	Rank
Bromomethane	1	Methyl *tert*-butyl ether	21
Dichlorodifluoromethane	2	Ethylene dibromide	22
1,1,1-Trichloroethane (TCA)	**3**	Styrene	23
Vinyl chloride	4	1,1-Dichloroethane	24
Chloroethane	5	1,2-Dichloroethane	25
Benzene	6	1,2-Dichloropropane	26
1,1-Dichloroethene	7	Carbon tetrachloride	26
Methylene chloride	**8**	1,2,4-Trimethylbenzene	28
Chlorobenzene	9	Bromodichloromethane	29
Trichloroethene (TCE)	**10**	Ethylbenzene	29
cis-1,2-Dichloroethene	11	Chloromethane	31
Toluene	12	*o*-Xylene	31
Diisopropyl ether	13	Isopropylbenzene	33
Trichlorofluoromethane	14	1,2-Dichlorobenzene	34
Trichlorotrifluoroethane	15	1,2,3-Trichloropropane	35
Perchloroethene (PCE)	**16**	*tert*-Amyl methyl ether	36
Bromoform	17	1,4-Dichlorobenzene	37
Dibromochloromethane	18	Ethyl *tert*-butyl ether	37
m- & *p*-Xylene	19	Naphthalene	39
Chloroform	20	*n*-Butylbenzene	40

Appendix 8.   Ranking of frequency of exceedance of Maximum Contaminant Levels for VOCs that had quantifiable concentrations in source water.

[Four solvents examined in this report are bolded]

VOC	Rank	VOC	Rank
Perchloroethene (PCE)	**1**	Benzene	[1]6
Trichloroethene (TCE)	**2**	Carbon tetrachloride	[1]6
1,1-Dichloroethene	3	Chlorobenzene	[1]6
Ethylene dibromide	3	**Methylene chloride**	[1]**6**
Vinyl chloride	5	Ethylbenzene	[1]6
1,1,1-Trichloroethane (TCA)	[1]**6**	Styrene	[1]6
1,1,2-Trichloroethane	[1]6	Toluene	[1]6
1,2,4-Trichlorobenzene	[1]6	*cis*-1,2-Dichloroethene	[1]6
1,2-Dichlorobenzene	[1]6	*trans*-1,2-Dichloroethene	[1]6
1,2-Dichloroethane	[1]6	Trihalomethanes	[1]6
1,2-Dichloropropane	[1]6	Xylenes	[1]6
1,4-Dichlorobenzene	[1]6		

[1]Frequency of exceedance was zero.

Appendix 9.   Ranking of median concentration of 44 VOCs that had quantifiable concentrations in drinking water, at an assessment level of 0.2 μg/L.

[Four solvents examined in this report are bolded]

VOC	Rank	VOC	Rank
Xylenes (mixed isomers)	1	Isopropylbenzene	23
Bromomethane	2	Ethylbenzene	24
1,2,4-Trimethylbenzene	3	**1,1,1-Trichloroethane (TCA)**	**25**
m- & *p-*Xylene	4	Bromoform	26
1,2-Dichloropropane	5	Carbon tetrachloride	26
*cis-*1,2-Dichloroethene	6	Dibromochloromethane	26
Chloroform	7	Dibromochloropropane	26
Trichloroethene (TCE)	**8**	1,1-Dichloroethane	30
1,2,3-Trichloropropane	9	**Methylene chloride**	**31**
*n-*Propylbenzene	9	1,2-Dichlorobenzene	32
Methyl *tert-*butyl ether	11	*n-*Butylbenzene	33
Perchloroethene (PCE)	**11**	Hexachlorobutadiene	34
Vinyl chloride	13	*o-*Xylene	34
Benzene	13	1,1-Dichloroethene	36
*trans-*1,2-Dichloroethene	15	1,2,4-Trichlorobenzene	37
Dichlorodifluoromethane	16	Chloroethane	37
Bromodichloromethane	17	1,4-Dichlorobenzene	39
Styrene	17	1,1,2-Trichloroethane	40
Toluene	17	1,2-Dichloroethane	40
Chloromethane	20	*cis-*1,3-Dichloropropene	42
Trichlorofluoromethane	21	Chlorobenzene	43
Naphthalene	22	Ethylene dibromide	44

Appendix 10.   Ranking of frequency of exceedance of Maximum Contaminant Levels for VOCs that had quantifiable concentrations in drinking water.

[Four solvents examined in this report are bolded]

VOC	Rank	VOC	Rank
Perchloroethene (PCE)	**1**	Benzene	[1]13
Trichloroethene (TCE)	**2**	**1,1,1-Trichloroethane (TCA)**	**[1]13**
1,1-Dichloroethene	3	1,1,2-Trichloroethane	[1]13
Trihalomethanes	4	1,2,4-Trichlorobenzene	[1]13
Ethylene dibromide	5	1,2-Dichlorobenzene	[1]13
Methylene chloride	**6**	1,4-Dichlorobenzene	[1]13
Vinyl chloride	7	Chlorobenzene	[1]13
1,2-Dichloropropane	8	Ethylbenzene	[1]13
cis-1,2-Dichloroethene	9	Styrene	[1]13
Dibromochloropropane	10	Toluene	[1]13
1,2-Dichloroethane	11	*trans*-1,2-Dichloroethene	[1]13
Carbon tetrachloride	11	Xylenes	[1]13

[1]Frequency of exceedance was zero.