Chapter 2—Introduction

Background and National Significance

1. What are VOCs?

VOCs are a subset of organic compounds with inherent physical and chemical properties that allow these compounds to move between water and air. This behavior is the fundamental basis for the USGS's laboratory analysis of VOCs in water samples, in which compounds that are sufficiently volatile are purged from a water sample by an inert gas and then identified and quantified by gas chromatography/mass spectrometry (GC/MS). In general, VOCs have high vapor pressures, low-to-medium water solubilities, and low molecular weights. Some VOCs may occur naturally in the environment, other compounds occur only as a result of manmade activities, and some compounds have both origins.

Volatile organic compounds (VOCs) are ground-water contaminants of concern because of very large environmental releases, human toxicity, and a tendency for some compounds to persist in and migrate with **ground water** to drinking-water supply wells (sidebar 1). Some VOCs, such as **chlorinated solvents**, have been used in commerce and industry for almost 100 years,[3] and chloroform and other **trihalomethanes (THMs)** have undoubtedly been present in chlorinated **drinking water** since the first continuous municipal application of chlorination in 1908.[4] The production and use of manmade organic compounds, many of which are classified as VOCs, increased by an order of magnitude between 1945 and 1985.[5] Some VOCs have had, and continue to have, very large and ubiquitous usage. An example is the widespread use of gasoline, which contains many VOCs. Furthermore, VOCs have had numerous uses in industry, commerce, households, and military sites (sidebar 2).

The presence of elevated concentrations of VOCs in drinking water may be a concern to human health.

The large-scale use of solutions of VOCs and products containing some VOCs has resulted in considerable quantities of VOCs released to the environment. Historically, many waste chemicals were disposed of indiscriminately. Because of this practice, VOCs often are the most frequently detected contaminants in soil and ground water at abandoned landfills and dumps, and at many industrial, commercial, and military sites across the Nation. Federal regulation of VOCs commenced in the 1970s with the passage of the Clean Air Act, Clean Water Act, Safe Drinking Water Act (SDWA), Resource Conservation and Recovery Act (RCRA), and other environmental acts. Collectively, much has been done in the past 30-plus years to mitigate pollution. Especially noteworthy examples for mitigating VOC ground-water contamination are (1) improved designs, operations, and disposal practices for the use of chlorinated **solvents** at industrial, commercial, and military sites; and (2) the cleanup of commercial gasoline release sites and the implementation of measures to minimize gasoline releases in the future. Despite these exemplary accomplishments, environmental releases of some VOCs from manufacturing facilities in the United States remain high. In 2001, for example, 4 of the 20 chemicals with the largest total on-site and off-site releases to the environment were VOCs, with a cumulative estimated release of more than 200 million pounds.[6]

The detection of VOCs in **aquifers** is important because of the widespread, large, and increasing use of ground water for drinking water. In 2000, about 50 percent of the Nation's population obtained their supply of drinking water from ground water (p. 28 and 29).

The presence of elevated VOC **concentrations** in drinking water may be a concern to human health because of their potential carcinogenicity. In addition to cancer risk, VOCs may adversely affect the liver, kidney, spleen, stomach, and heart, as well as the nervous, circulatory, reproductive, and respiratory systems. Some VOCs may affect cognitive abilities, balance, or coordination, and some are eye, skin, and/or throat irritants. Because of known or suspected human-health concerns, the USEPA has established **Maximum Contaminant Levels (MCLs)** that apply to 29 VOCs in drinking water supplied by **public water systems (PWSs)**. In addition, some States have set MCLs for additional VOCs and in some cases have established more stringent standards than the USEPA values. The human-health consequences of low-concentration exposure of VOCs in drinking water (that is, at concentrations less than MCLs) are uncertain.

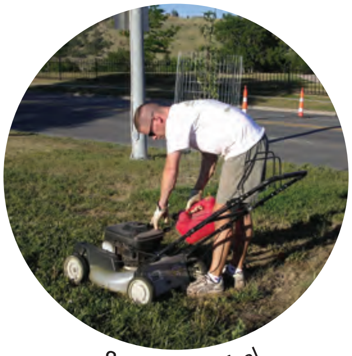
2. How are VOCs Used?

VOCs have been used extensively in the United States since the 1940s. VOCs are common components or additives in many commercial and household products including gasoline, diesel fuel, other petroleum-based products, carpets, paints, varnishes, glues, spot removers, and cleaners. Example industrial applications include the manufacturing of automobiles, electronics, computers, wood products, adhesives, dyes, rubber products, and plastics, as well as in the synthesis of other organic compounds. VOCs also are used in the dry cleaning of clothing, in refrigeration units, and in the degreasing of equipment and home septic systems. VOCs are present in some personal care products such as perfumes, deodorants, insect repellents, skin lotions, and pharmaceuticals. Some VOCs also have been applied as **fumigants** in agriculture and in households to control insects, worms, and other pests.

The detection of VOCs in ground water is a concern to officials involved in the management of aquifers because such an occurrence implies aquifer vulnerability.

In addition to human-health concerns, scientists and engineers involved in the management of aquifers and water-supply development are concerned about the detection of VOCs in ground water because such an **occurrence** implies aquifer **vulnerability**. Identifying additional source-control strategies or enhancing existing measures may be warranted if **anthropogenic compounds** are detected frequently in ground water. The detection of a VOC in ground water also may be of concern because it denotes that a pathway exists by which other persistent and potentially toxic compounds may reach drinking-water supply wells.


Automotive painting


Small engine fuel


Paint stripping

Products containing VOCs have many uses in commerce and households. (Photographs by: left, Connie J. Ross; middle, Janet M. Carter; right, Rika Lashley, U.S. Geological Survey.)

This Assessment's Purpose and Scope

3. Assessing the Quality of Ground Water

Ground water is an important supply of drinking water in the United States, and the study of aquifers is a large component of NAWQA's ground-water assessments. Aquifer studies have been completed in nearly every NAWQA **Study Unit** and have provided a comprehensive picture of the chemical quality of water in locally and regionally important aquifers. More information on specific aquifer studies is available on the Circular's Web site.

Many pesticides, VOCs, nutrients, and naturally occurring chemicals are monitored in aquifer studies. Typically the aquifer (or portion thereof) selected for study is locally one of the most intensively used aquifers for drinking water. Aquifer studies are designed to provide an overall picture of the aquifer's water-quality condition and, as such, are considered resource assessments. To achieve this spatially large aquifer characterization, wells selected for sampling are randomly located but distributed approximately equally across the study area. A variety of well types with different water uses are included in the assessment of aquifer studies. None of the sampled wells were selected because of prior knowledge of nearby contamination.

VOCs were selected for emphasis in the USGS's NAWQA Program primarily because of the previously reported occurrence of some of these compounds in many of the Nation's water supplies.[3, 7, 8, 9, 10] The overall intent of the Program's VOC assessment is to provide an improved understanding of the occurrence and geographical distribution of selected VOCs in the Nation's water resources, with emphasis on ground water. The assessment includes both new VOC data collected in the Program's **Study-Unit investigations** and VOC data from previous studies with a similar design.

Previous findings from the Program's assessment of VOCs were reported initially in 1999 with emphasis on (1) the occurrence of VOCs in samples from wells in **urban** and **rural areas**; and (2) the probability of detecting one or more VOCs in ground water on the basis of population density.[11] Subsequently, the Program's scientists have reported national-scale occurrence findings for (1) mixtures of VOCs, pesticides, and nitrate in samples from **domestic** and **public wells**;[12] (2) VOCs in the water supply of selected **community water systems (CWSs)**;[13, 14] (3) MTBE and **gasoline hydrocarbons** in ground water;[15] and (4) VOCs in domestic well samples[16] and in shallow, urban ground water.[17]

The overall intent of the NAWQA Program's VOC assessment is to provide an improved understanding of the occurrence and distribution of selected VOCs in the Nation's water resources.

This report presents additional salient findings of the national VOC assessment and gives emphasis to the occurrence of VOCs in the Nation's ground water (sidebar 3) and in samples from drinking-water supply wells (sidebar 4). This includes information about the **detection frequency**, concentration, geographical distribution, and mixtures of VOCs. Also described are natural and **anthropogenic** factors that were found to be associated with the occurrence of some of the frequently detected VOCs. Additionally, this report presents information and more in-depth findings for selected VOCs including (1) chloroform and other THMs; (2) chlorinated solvents—methylene chloride, PCE, 1,1,1-trichloroethane (TCA), and TCE; (3) MTBE and other **gasoline oxygenates**; and (4) gasoline hydrocarbons.

Information on the occurrence of VOCs is presented separately in this report for ground water (Chapter 3) and drinking-water supply wells, specifically domestic and public wells (Chapter 4). It is recognized that various agencies, organizations, researchers, resource managers, decision makers, and the public have different interests and information needs regarding the use and management of ground-water resources and the protection and oversight of drinking-water supplies. NAWQA **aquifer studies** are large-scale resource assessments of ground water that provide a general characterization of water-quality conditions in locally important aquifers or portions thereof. When completed in many locations, these studies collectively provide an important national perspective on the current extent of VOC contamination and regional patterns of VOC occurrence in ground water. In addition, aquifer studies characterize the vulnerability of ground-water systems to VOCs, as well as to other contaminants with similar sources and environmental properties. This information may be especially valuable for national and regional decisions about the need for future ground-water protection and associated policies and regulations.

The primary purpose of this report is to present important findings of the assessment of VOCs in the Nation's ground water and drinking-water supply wells.

The occurrence of VOCs in samples from domestic and public wells is presented separately in order to distinguish the separate issues for these well types related to supply, environmental setting, and sources of VOCs. Samples from these wells provide information about VOC contamination that may reach tap water unless the supply is treated to remove any VOCs or is diluted with other water supplies. Occurrence information for individual VOCs provides important insights about the **concentrations of potential human-health concern** in drinking-water supply wells and the need for controlling their sources of contamination. This information often is sought by water utilities, public health agencies, the public, and rural citizens who rely on private wells for drinking water.

A total of 55 VOCs are included in this assessment, and a sample from each well was routinely analyzed for nearly all of these compounds. The selection procedure for the inclusion of these VOCs in NAWQA's routine monitoring is described elsewhere[18] and included, for example, consideration of the feasibility of laboratory analysis, known or suspected human-health concerns, frequency of occurrence in water resources based on prior investigations, and potential for large-scale use.

Example Key Questions About VOCs That NAWQA's Findings Address:

- Which VOCs are detected most frequently in aquifers? In samples from domestic and public wells? At what concentrations?
- Which of the aquifers studied are most vulnerable to VOC contamination?
- Which natural and anthropogenic factors are associated with VOC occurrence in aquifers and samples from domestic and public wells?
- Are the frequently detected VOCs found everywhere in aquifers across the Nation or are local/regional occurrence patterns evident?
- Are specific mixtures of VOCs common? Which mixtures occur most frequently?
- Do domestic or public wells have more low-level VOC contamination? Why?
- Which VOCs are detected at concentrations of potential human-health concern in samples from domestic and public wells?
- Which VOC occurrence findings provide insights for future ground-water protection?

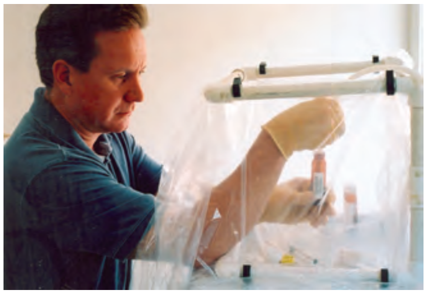
4. Assessing the Quality of Ground Water Captured by Drinking-Water Supply Wells

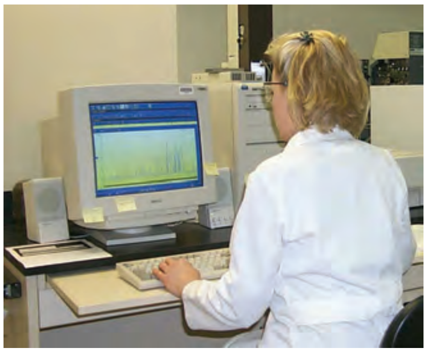
NAWQA's studies of drinking-water supply wells focus on the quality of ground water captured by domestic and public wells, in contrast to the quality of tap water (that is, drinking water). USGS field personnel collect samples of ground water from domestic and public wells at the wellhead and before any treatment or blending. As such, NAWQA's studies complement drinking-water-compliance-monitoring programs required by other agencies; these programs usually specify monitoring after treatment or blending. Comparisons of concentrations for domestic and public **well samples** to **primary drinking-water standards** and **Health-Based Screening Levels (HBSLs)** in this report are made only in the context of the quality of untreated and unblended ground water. Human exposure from tap water and other pathways is not quantified.

During NAWQA's first decade of assessments, many domestic wells and some public wells were sampled. During its second decade, additional emphasis has been placed on understanding the quality of drinking-water supplies including the monitoring of river intakes and production wells of large CWSs, as well as the continued sampling of domestic wells. In addition, major factors that influence the transport of chemicals to public wells are being studied.

Studies of drinking-water supplies are important because these studies (1) identify the presence and concentrations of those chemicals that may reach domestic and public wells (or surface-water intakes); and (2) provide information on the need for enhanced source control. Through these studies, the USGS will continue to collaborate with other agencies, organizations, and water utilities involved with the supply of the Nation's drinking water.

This Assessment's Approach





Samples for VOC determination are collected and analyzed by established methods that ensure high-quality occurrence information. (Photographs by Barbara L. Rowe, U.S. Geological Survey.)

This section describes some aspects of the assessment's approach. Additional details are presented elsewhere[(19)] and in Appendix 3. Two primary objectives of this assessment included determination of (1) VOCs in **ambient ground water** from aquifer studies; and (2) VOCs in samples from actively used domestic and public wells. Samples from 3,498 wells with a variety of water uses were selected for analysis of VOCs in aquifer studies (table 1). VOC data from 2,401 domestic wells and 1,096 public wells were available from aquifer studies, **shallow ground-water studies**, and a national source-water survey (table 2) to characterize the occurrence of VOCs in these two well types. One VOC analysis per well was included in the assessment. Well selection criteria and maps showing the locations of wells are presented in Appendix 3.

VOC data for domestic well samples are a large subset of data for aquifer studies because existing wells, including many domestic wells, were selected for sampling. Domestic wells commonly were chosen for aquifer studies because their distribution in most areas best fit the study objective of assessing the quality of aquifers using randomly selected and spatially distributed sampling points for a large area.

All samples for NAWQA studies were collected and analyzed by USGS personnel using approved USGS methods. For nearly all of the ground-water samples analyzed by the USGS, compounds were identified and concentrations were quantified using GC/MS. For data not collected or analyzed by USGS, laboratory certification and use of GC/MS methods were required for inclusion of data in this assessment.

Table 1. Number of wells with VOC data for aquifer studies by water use.

Use of water	Aquifer studies	
	Number of wells	Percent of wells
Domestic supply	2,138	61.1
Public supply	513	14.7
Monitoring	335	9.6
Other	461	13.2
Unknown	51	1.5
Total	3,498	100

Table 2. Number of domestic and public wells with VOC data by data source.

Data source	Domestic wells		Public wells	
	Number of wells	Percent of wells	Number of wells	Percent of wells
Aquifer studies	[1]2,138	89.0	[1]513	46.8
Shallow ground-water studies	263	11.0	8	.7
National source-water survey	0	0	575	52.5
Total	2,401	100	1,096	100

[1]Same wells used in aquifer studies (table 1).

As noted previously, 55 VOCs were included in this assessment. These VOCs were assigned to the following groups on the basis of their primary usage (or origin): (1) fumigants, (2) gasoline hydrocarbons, (3) gasoline oxygenates, (4) **organic synthesis compounds**, (5) **refrigerants**, (6) solvents, and (7) THMs (chlorination **by-products**). Other uses and additional information for the 55 VOCs can be found in Appendix 4.

Various quality-control criteria were used to select wells and VOC data for this national assessment.

Most detection frequencies were computed by applying an **assessment level** of 0.2 μg/L (sidebar 5). The assessment level of 0.2 μg/L was chosen to represent the laboratory reporting value for USGS prior to April 1996 and to be compatible with other agencies. For this assessment level, data from all sampled wells were used in the computation of detection frequencies. The number of samples with laboratory analyses varied among the 55 VOCs.

For some computations, an assessment level of 0.02 μg/L also was applied. This assessment level was selected to represent the occurrence of VOCs using a new, **low-level analytical method** developed by the USGS for natural waters. When applying this assessment level for aquifer studies, the samples from a subset of 1,687 wells that were analyzed using the new method were used in the computation of detection frequencies. Data from a subset of 1,208 wells were available for computations for domestic well samples; however, insufficient data were available for computations for public well samples at an assessment level of 0.02 μg/L.

A variety of ancillary data and statistical models were used to relate the occurrence of VOCs to various hydrogeologic and anthropogenic variables. The hydrogeologic variables that were used in the relational analyses represented the transport and fate of VOCs in ground water. The anthropogenic variables used in the relational analyses represented some of the potential sources of VOCs to ground water. A listing of the ancillary data used in these analyses can be found elsewhere.[19]

For those compounds with Federal drinking-water standards, VOC concentrations in samples from domestic and public wells were compared to USEPA MCLs. Concentrations for 15 **unregulated compounds** were compared to HBSLs (p. 30), which were developed by the USGS in collaboration with the USEPA, New Jersey Department of Environmental Protection, and the Oregon Health & Science University. HBSLs are not enforceable regulatory standards but are concentrations of contaminants in water that warrant scrutiny because they may be of potential human-health concern.[20]

5. What are Assessment Levels, and Why are They Used?

The detection frequency of VOCs in ground water is an important indicator of water quality in occurrence assessments. In order to compare detection frequencies for individual VOCs, groups of VOCs, or VOC data from different agencies with different reporting levels, an "assessment level" must be established. An assessment level is a fixed concentration that is the basis for computing detection frequencies.

An assessment level is necessary because the detection frequency computed for a specific VOC depends on the **laboratory reporting level** for that compound.[21] Laboratory reporting levels for VOCs may vary from compound to compound and from one laboratory to another due to differences in laboratory equipment, equipment sensitivity, experience and skill of equipment operators, or laboratory conditions. In addition, data sets collected for different monitoring objectives or analyzed by different laboratory methods also can have different reporting levels. Thus, different detection frequencies for VOC data sets with different reporting levels may not represent true differences in water quality, but rather they may only reflect the above noted factors.

Sources, Transport, and Fate of VOCs in Ground Water—An Overview

6. How Do Ground-Water Concentrations from VOC Sources Differ?

VOC contamination can originate from the release of liquids, such as petroleum hydrocarbons or solvents, at one location. The release of VOCs from a LUST is an example of such contamination and commonly results in concentrations of VOCs in ground water near the source at the milligram or gram per liter level. These large concentrations are one reason why this type of contamination can spread over a large area.

Contamination also can originate over large areas from sources such as leaking water and sewer lines, stormwater runoff, and **atmospheric deposition**. Typically, these sources result in small concentrations (microgram per liter or smaller) in water.

VOCs are used in numerous industrial, commercial, and domestic applications and can contaminate ground water through sources such as landfills and dumps, leaking storage tanks, septic systems, leaking water and sewer lines, stormwater runoff, and the atmosphere. These sources differ, however, in their potential to cause elevated concentrations of VOCs in ground water (sidebar 6). Many household products contain VOCs and can be discarded to septic systems or disposed of improperly. In commerce and industry, VOCs are used in numerous applications (sidebar 2), and these uses result in considerable quantities of VOCs being released to the environment.[(22)] Once in the environment, many VOCs move between the atmosphere, soil, ground water, and surface water. Although many VOCs have relatively short **half-lives** in certain media because of **degradation**, other VOCs such as DBCP, TCA, and MTBE can persist in ground water and degrade only slightly over a period of years or decades.

Manmade structures, such as recharge basins and shallow injection wells, can hasten the transport of VOCs to ground water.

VOCs can be transported through the **unsaturated zone** in **recharge**, in soil vapor, or as a **non-aqueous-phase liquid**. Any hydrologic condition that shortens residence time within the unsaturated zone can result in increased amounts of VOCs to the water table; for example, manmade structures like recharge basins and shallow injection wells can accelerate transport through the unsaturated zone. Furthermore, a shallow water table and abundant recharge will favor more rapid transport through the unsaturated zone and increase the likelihood of VOCs reaching ground water. Some VOCs also can move slowly through the unsaturated zone with air and enter the top of the water table by partitioning between soil air and ground water; however, this type of transport also is enhanced by the movement of recharge.[(23)]

The movement of solutes by the bulk motion of flowing ground water is known as **advection**. The rate of advective transport varies by many orders of magnitude.[(24)] The tendency of solutes to spread out from the path that would be expected from advective flow is known as **dispersion**. VOCs in ground water can eventually be captured by pumping wells or discharged to surface waters if traveltimes are short enough to prevent the complete attenuation of VOCs.

The transport of VOCs dissolved in ground water also may be slowed by **sorption** to organic carbon in the aquifer material. The effect of sorption on VOC transport is dependent on the solubility of the VOC, the amount of organic carbon in the aquifer, and aquifer density and porosity. Some very

A possible source of VOCs is illustrated by the leaking barrels from a Superfund site. (Photograph courtesy of U.S. Environmental Protection Agency.)

soluble VOCs like MTBE have a small sorption tendency and thus move as quickly as ground water, whereas other less soluble VOCs like carbon tetrachloride have a larger sorption tendency and may move slowly relative to the rate of ground-water flow.[25]

Some VOCs, such as DBCP, TCA, and MTBE, can persist in ground water with little degradation over years or decades.

The fate of VOCs in ground water is largely dependent on their persistence under the conditions present in the aquifer. VOCs that are persistent in water are more likely to be detected in ground water because they can travel greater distances from their source before degradation and dilution occur. In ground water, VOCs may undergo selective **abiotic** (not involving microorganisms) and **biotic** (involving microorganisms such as bacteria and fungi) degradation. An example of **abiotic degradation** is the degradation of TCA to 1,1-dichloroethene (1,1-DCE) by reaction with water. For most VOCs, **biotic degradation** generally is more important than abiotic degradation. Some VOCs can be degraded biotically under a range of **redox conditions**,[25] whereas others may persist in ground water until a particular redox condition occurs. An example of biotic degradation is the degradation of PCE to TCE.

Bacteria may be unable to use VOCs as a sole source of food when the compounds are present at nanogram per liter or low microgram per liter concentrations.[26] This may slow the degradation of VOCs in ground water. A decline in the degradation rate with decreasing concentration may account for the low VOC concentrations detected in this assessment for some VOCs that degrade quickly at larger concentrations.

VOCs can be transported with precipitation to ground water and stormwater runoff. (Bottom photograph by Charles G. Crawford, U.S. Geological Survey.)

Two other possible sources of VOCs are demonstrated by contamination originating from automobiles and this leaking underground storage tank. (Bottom photograph courtesy of the Utah Department of Environmental Quality.)

Chapter 2