

Chapter 1—Major Findings and Conclusions

This national assessment of 55 volatile organic compounds (VOCs) in ground water gives emphasis to the occurrence of VOCs in aquifers that are used as an important supply of drinking water. In contrast to the monitoring of VOC contamination of ground water at point-source release sites, such as landfills and leaking underground storage tanks (LUSTs), our investigations of aquifers are designed as large-scale resource assessments that provide a general characterization of water-quality conditions. Nearly all of the aquifers included in this assessment have been identified as regionally extensive aquifers or aquifer systems.⁽²⁾ The assessment of ground water (Chapter 3) included analyses of about 3,500 water samples collected during 1985–2001 from various types of wells, representing almost 100 different aquifer studies. This is the first national assessment of the occurrence of a large number of VOCs with different uses, and the assessment addresses key questions about VOCs in aquifers. The assessment also provides a foundation for subsequent decadal assessments of the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program to ascertain long-term trends of VOC occurrence in these aquifers.

The occurrence of VOCs in samples collected from drinking-water supply wells, specifically domestic and public wells, also is included (and discussed separately from aquifer studies) in this assessment (Chapter 4), recognizing

that various agencies, organizations, decision makers, and others have different interests and information needs. Occurrence findings are compared between domestic and public wells to distinguish the separate issues for these well types related to supply, environmental setting, and sources of VOCs. For this purpose, the occurrence of 55 VOCs is based on analyses of samples collected at the well head, and before any treatment or blending, from about 2,400 domestic wells and about 1,100 public wells. Findings from domestic well samples update earlier USGS studies and provide improved national coverage of sampled wells. As such, this assessment provides important information on VOC occurrence for domestic well samples that may be useful to public health agencies. Findings for public well samples constitute the most current understanding of the occurrence of a large number of VOCs in untreated ground water used by public water systems (PWSs) across the Nation. Our assessment of public well water complements compliance monitoring by water utilities that typically focus on drinking water delivered to the public.

Major findings that may be most relevant to the management and monitoring of the Nation's ground water and drinking-water supply wells are emphasized in the following discussion. Additional information is included in subsequent chapters of this report and at a supporting Web site (http://water.usgs.gov/nawqa/vocs/national_assessment).



Some household products contain VOCs or chemicals that form VOCs when added to water. (Photograph courtesy of Joel Beamer, professional photographer.)

VOCs were detected in many aquifers across the Nation. Almost 20 percent of the water samples from aquifers contained one or more of the 55 VOCs, at an assessment level of 0.2 microgram per liter ($\mu\text{g/L}$). This detection frequency increased to slightly more than 50 percent for the subset of samples analyzed with a low-level analytical method and for which an order-of-magnitude lower assessment level ($0.02 \mu\text{g/L}$) was applied. VOCs were detected in 90 of 98 aquifer studies completed across the Nation, with most of the largest detection frequencies in California, Nevada, Florida, and the New England and Mid-Atlantic States. Trihalomethanes (THMs), which may originate as chlorination by-products, and solvents were the most frequently detected VOC groups. Furthermore, detections of THMs and solvents and some individual compounds were geographically widespread; however, a few compounds, such as methyl *tert*-butyl ether (MTBE), ethylene dibromide (EDB), and dibromochloropropane (DBCP), had regional or local occurrence patterns. The widespread occurrence of VOCs indicates the ubiquitous nature of VOC sources and the vulnerability of many of the Nation's aquifers to low-level VOC contamination. The findings for VOCs indicate that other compounds with widespread sources and similar behavior and fate properties also may be occurring. (See p. 16, 18, 20, and 21.)

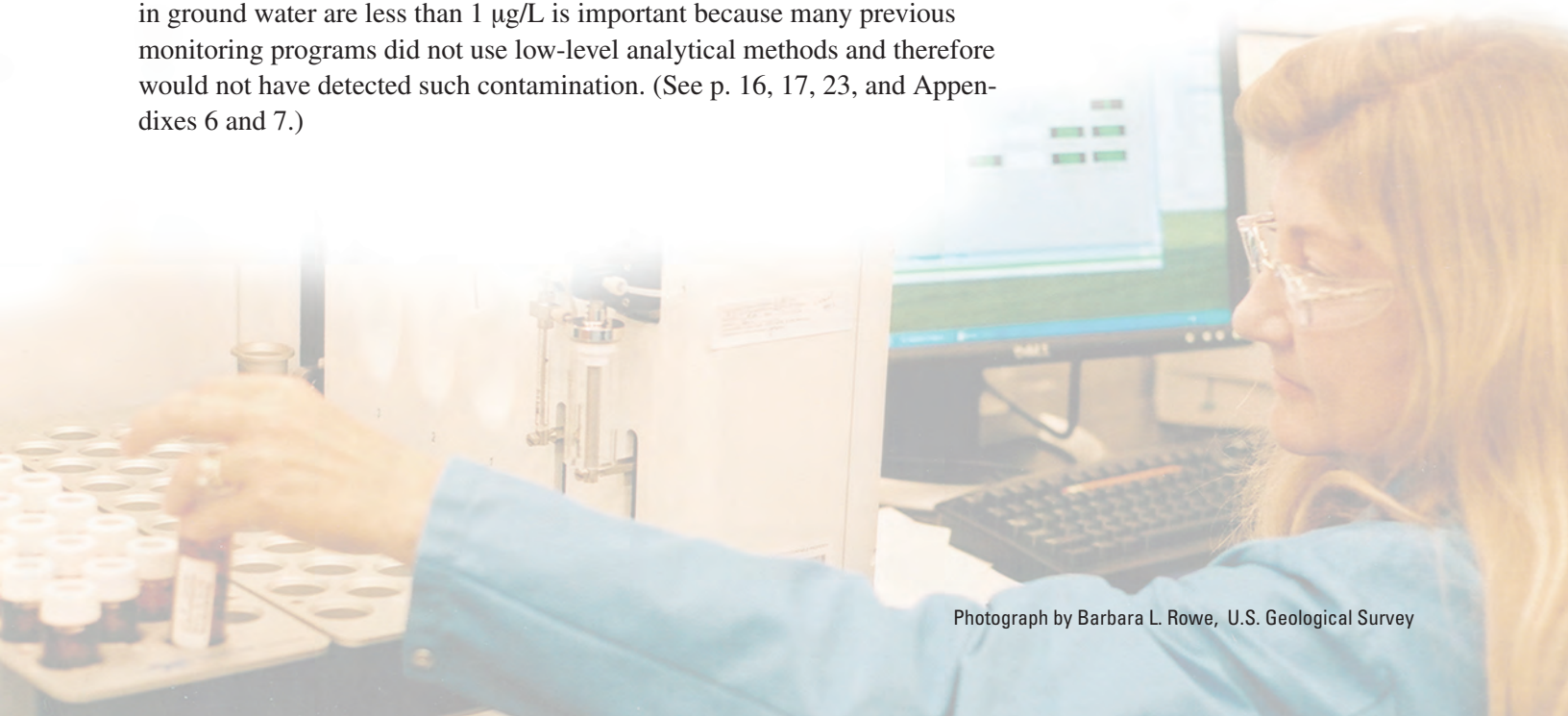
Many VOCs were detected, but typically at low concentrations. In water samples from aquifers, the concentrations of each VOC and the total concentration of all VOCs analyzed generally were low (defined in this report as concentrations less than $1 \mu\text{g/L}$). For example, 90 percent of the total VOC concentrations in samples were less than $1 \mu\text{g/L}$. Forty-two of the 55 VOCs were detected in one or more samples at an assessment level of $0.2 \mu\text{g/L}$. Furthermore, VOCs in each of the seven VOC groups considered in this assessment were detected in the samples; these groups included fumigants, gasoline hydrocarbons, gasoline oxygenates, organic synthesis compounds, refrigerants, solvents, and THMs. The finding that most VOC concentrations in ground water are less than $1 \mu\text{g/L}$ is important because many previous monitoring programs did not use low-level analytical methods and therefore would not have detected such contamination. (See p. 16, 17, 23, and Appendixes 6 and 7.)

CONCLUSIONS

- Many of the Nation's aquifers are vulnerable to low-level VOC contamination, indicating the need to include VOCs in ground-water monitoring programs to track the trend of the low-level VOC contamination identified in this assessment.
- It is important to continue to control sources of VOCs, as well as to enhance information about the location, composition, and other characteristics of VOC releases that may affect ground water.

CONCLUSION

- VOC contamination in aquifers may be more prevalent than previously reported in monitoring programs that used analytical methods with higher reporting levels.



Photograph by Barbara L. Rowe, U.S. Geological Survey

Some VOCs were detected more frequently than others. Although 42 VOCs were detected in aquifer samples, only 15 occurred in about 1 percent or more of the samples. The most frequently detected VOCs include 7 solvents, 4 THMs, 2 refrigerants, 1 gasoline oxygenate, and 1 gasoline hydrocarbon. The THM chloroform was the most frequently detected compound, and its source is attributed, in part, to the recycling of chlorinated waters to aquifers. The solvent perchloroethene (PCE) and the gasoline oxygenate MTBE were the second and third most frequently detected compounds, respectively. Overall, the 15 most frequently detected compounds comprise a large fraction of the low-level VOC contamination and provide a logical focus for future monitoring of aquifers and for follow-up studies to better understand their sources and pathways to aquifers. (See p. 22 and Appendix 6.)

VOCs found in about 1 percent or more of aquifer samples, at an assessment level of 0.2 µg/L (compounds listed by decreasing detection frequency)

Compound name	VOC group
Chloroform	trihalomethane
Perchloroethene	solvent
Methyl <i>tert</i> -butyl ether	gasoline oxygenate
Trichloroethene	solvent
Toluene	gasoline hydrocarbon
Dichlorodifluoromethane	refrigerant
1,1,1-Trichloroethane	solvent
Chloromethane	solvent
Bromodichloromethane	trihalomethane
Trichlorofluoromethane	refrigerant
Bromoform	trihalomethane
Dibromochloromethane	trihalomethane
<i>trans</i> -1,2-Dichloroethene	solvent
Methylene chloride	solvent
1,1-Dichloroethane	solvent

Explaining VOC contamination in aquifers is complex—VOC occurrence is determined not only by sources but also by natural and anthropogenic factors that affect the transport and fate of VOCs in aquifers. The complexity of explaining VOC contamination in aquifers was affirmed in this assessment through statistical models for 10 frequently detected compounds. Factors describing the source, transport, and fate of VOCs were all important in explaining the national occurrence of these VOCs. For example, the occurrence of PCE was statistically associated with the percentage of urban land use and density of septic systems near sampled wells (source factors), depth to top of well screen (transport factor), and presence of dissolved oxygen (fate factor). National-scale statistical analyses provide important insights about the factors that are strongly associated with the detection of specific VOCs, and this information may benefit many local aquifer investigations in selecting compound- and aquifer-specific information to be considered. Continued efforts to reduce or eliminate low-level VOC contamination will require enhanced knowledge of sources of contamination and aquifer characteristics. (See p. 24 and 25.)

Factors most commonly associated with VOCs in aquifers

• Septic systems
• Urban land
• Resource Conservation and Recovery Act (RCRA) hazardous-waste facilities
• Gasoline storage and release sites
• Climatic conditions
• Hydric (anoxic) soils
• Dissolved oxygen in ground water
• Type of well
• Depth to top of well screen

CONCLUSIONS

- Future studies to understand how VOC contamination of aquifers is occurring can focus on relatively few compounds.
- Additional source control and/or remediation measures, if deemed warranted, also can focus on relatively few compounds, yet would address much of the low-level VOC contamination evident in this assessment.

CONCLUSIONS

- The natural and anthropogenic factors important to VOC occurrence in a particular aquifer need to be understood in order to effectively manage and protect aquifers that are susceptible to VOC contamination.
- A careful review of the importance and feasibility of further reducing or eliminating VOC sources to aquifers also is needed to manage and protect these aquifers.

Despite the short period of its extensive use, MTBE was one of the most frequently detected VOCs. As noted previously, MTBE was the third most frequently detected VOC in aquifers. MTBE production peaked in the 1990s with the majority of it used voluntarily by refineries for the Nation's Reformulated Gasoline (RFG) Program. Concentrations of MTBE in aquifer samples were rarely of concern relative to the U.S. Environmental Protection Agency's (USEPA) drinking-water advisory based on taste and odor; however, MTBE concentrations in ground water were detected more frequently in RFG Program areas than in other areas. The relatively frequent detection of MTBE in aquifers was not an anticipated outcome at the commencement of NAWQA's assessment because of MTBE's short and recent use. A period of only a decade or less was required for the detection of MTBE in some of the Nation's aquifers. MTBE findings demonstrate how quickly some anthropogenic chemicals, especially those that are mobile and persistent like MTBE, may reach aquifers that are especially susceptible to land-surface or atmospheric contamination. (See p. 22, 50–53.)

Some VOCs were not detected in aquifer samples. Thirteen of the VOCs included in this national assessment were not detected in any aquifer samples at a concentration of 0.2 µg/L or larger. The 13 compounds include 5 VOCs predominantly used in organic synthesis, 4 solvents, 2 fumigants, 1 gasoline hydrocarbon, and 1 gasoline oxygenate. The specific reason(s) why each of these compounds was not detected has not been ascertained; however, their lack of occurrence likely is attributed to one or more of the following factors: (1) limited use in industry, commerce, and household products; (2) small releases to water and land; (3) most use occurs in controlled industrial processes or in organic synthesis; (4) the compound degrades quickly to other compounds in the environment; and (5) insufficient time has elapsed to allow the compound to reach wells sampled in this assessment. (See Appendix 6.)

VOCs not detected in aquifer samples, at an assessment level of 0.2 µg/L (compounds listed by VOC group)

Compound name	VOC group
Acrolein	organic synthesis compound
Acrylonitrile	organic synthesis compound
Hexachlorobutadiene	organic synthesis compound
1,2,3-Trichlorobenzene	organic synthesis compound
Vinyl bromide	organic synthesis compound
1,3-Dichlorobenzene	solvent
Hexachloroethane	solvent
1,2,4-Trichlorobenzene	solvent
1,1,2-Trichloroethane	solvent
<i>cis</i> -Dichloropropene	fumigant
<i>trans</i> -Dichloropropene	fumigant
Styrene	gasoline hydrocarbon
Ethyl <i>tert</i> -butyl ether	gasoline oxygenate

CONCLUSIONS

- Some VOCs that are mobile and persistent may reach especially susceptible aquifers within a decade or less of extensive use, and potentially adversely affect ground-water quality.
- The environmental behavior and fate properties of anthropogenic compounds should be included in decision-making processes prior to their approval for large-scale commercial, industrial, and other uses.

CONCLUSION

- Some of these VOCs may not warrant continued inclusion in large-scale resource assessments, such as aquifer studies completed in the NAWQA Program, if it is confirmed that their use, release, and behavior and fate characteristics pose a small or negligible likelihood of ground-water contamination.

Although VOCs were detected frequently in samples from domestic and public wells, only a small percentage of samples had VOC concentrations of potential human-health concern. One or more VOCs were detected in about 14 and 26 percent of domestic and public well samples, respectively, at an assessment level of 0.2 µg/L. However, only about 1 to 2 percent of domestic and public well samples had concentrations of potential human-health concern (defined in this report as concentrations greater than a USEPA Maximum Contaminant Level (MCL) or concentrations greater than a Health-Based Screening Level (HBSL) for compounds without an MCL). Eight compounds were detected at concentrations of potential concern, and three of these compounds occurred in both domestic and public well samples. Most of the concentrations of potential concern were attributed to the fumigant DBCP (in domestic well samples only) and the solvents PCE and trichloroethene (TCE) in samples from both well types. Because NAWQA's assessment is based on samples collected at the wellhead, it is unknown if those domestic and public well samples with concentrations of potential concern actually result in concentrations greater than MCLs in drinking water. (See p. 30–35.)

VOCs found at concentration(s) of potential human-health concern (compounds listed by decreasing number of concentrations of potential concern).

Compound name	VOC group	Domestic wells	Public wells
Trichloroethene	solvent	X	X
Dibromochloropropane	fumigant	X	
Perchloroethene	solvent	X	X
1,1-Dichloroethene	organic synthesis compound	X	X
1,2-Dichloropropane	fumigant	X	
Ethylene dibromide	fumigant	X	
Methylene chloride	solvent		X
Vinyl chloride	organic synthesis compound		X

Additional VOCs may warrant inclusion in a low-concentration, trends-monitoring program. Nine VOCs that did not occur at concentrations of potential concern in samples from domestic and/or public wells were detected at concentrations below but within a factor of 10 of an MCL. The 9 compounds include 4 solvents, 4 THMs, and 1 gasoline hydrocarbon. These 9 VOCs, plus the 8 compounds with concentrations of potential concern, are important compounds to consider including in a low-concentration, trends-monitoring program, such as the NAWQA Program. Such programs seek to identify compounds in domestic and public well samples before concentrations reach levels of potential concern. Also noteworthy is the finding that the solvents PCE and TCE had, relative to other VOCs, a large number of concentrations in both domestic and public well samples below but within a factor of 10 of their MCLs. (See p. 32, 34, and Appendixes 9 and 11.)

Additional VOCs that may warrant inclusion in a low-concentration, trends-monitoring program (compounds listed by VOC group)

Compound name	VOC group
Benzene	gasoline hydrocarbon
Carbon tetrachloride	solvent
1,2-Dichloroethane	solvent
<i>cis</i> -1,2-Dichloroethene	solvent
1,1,1-Trichloroethane	solvent
Bromodichloromethane	trihalomethane
Bromoform	trihalomethane
Chloroform	trihalomethane
Dibromochloromethane	trihalomethane

CONCLUSIONS

- Most samples from domestic and public wells had VOC concentrations less than MCLs and HBSLs, indicating that these concentrations are not anticipated to cause adverse human-health effects.
- Some samples had VOC concentrations greater than MCLs, indicating possible adverse human-health effects if drinking water with these concentrations was consumed over a lifetime. However, there are uncertainties about actual drinking-water exposure and health effects of water from these supply wells. Further study of these wells is warranted to understand contaminant sources and VOC concentrations in drinking water.

CONCLUSIONS

- Comparing concentrations to MCLs and HBSLs helps prioritize which compounds merit further study or monitoring. This assessment identified 17 VOCs that may warrant consideration for inclusion in a low-concentration, trends-monitoring program for domestic and public wells.
- NAWQA's occurrence information for these 17 compounds is important information considered in the USEPA's Contaminant Candidate List (CCL) Program.
- Because of the relatively large number of concentrations near and greater than their MCLs, the solvents PCE and TCE appear to warrant special emphasis to understand their sources and their capture by both domestic and public wells.

In general, public wells are more vulnerable to low-level VOC contamination than are domestic wells. The detection frequencies of nearly all of the most frequently detected compounds and mixtures of VOCs were larger in samples from public wells than from domestic wells, at an assessment level of 0.2 $\mu\text{g/L}$. Mixtures of 2 or more of the 55 VOCs were found in about 13 percent of the public well samples—more than three times more frequently than in domestic well samples—and the likelihood of detecting a mixture of VOCs in public well samples was about the same as detecting a single compound. Furthermore, 10 of the 15 most frequently detected VOCs in public well samples were either THMs or solvents, and all but one of the most common VOC mixtures included THMs. The larger detection frequencies in public well samples than in domestic well samples is attributed, in part, to the larger withdrawal rates of public wells and their proximity to developed areas. The larger pumping rates may increase the capture and movement of VOC contamination to public wells. The proximity of public wells to developed areas increases the likelihood of VOC sources. (See p. 36–41.)

Water that has been chlorinated or exposed to household products containing chlorine is an important source of chloroform and possibly other compounds in ground water supplying domestic and public wells. Chloroform was the most frequently detected VOC in domestic and public well samples. The chloroform detected in ground water may have potential sources associated with its use as a solvent and an extractant, and as an intermediate product in organic synthesis. Also, chloroform and other THMs are by-products of the chlorination of drinking waters and wastewaters, and the disinfection of domestic and public wells. These compounds also may be present in the effluent of septic systems from the use of household products containing chlorine, such as bleach. Furthermore, artificial recharge of chlorinated water containing THMs and potentially other compounds is becoming more common, especially in western States due to, in part, the limited supply of drinking water. The chlorination of water to control water-borne diseases has been a common practice in the United States for nearly a century. This long-term use has allowed ample time for the recharge of waters containing THMs to reach many of the sampled wells. Once introduced to ground water, chloroform and other THMs may persist and move long distances in some aquifers. The relative detection frequencies of the THMs in well samples, and the common occurrence of mixtures of THMs in public well samples, indicate that waters with a history of chlorination and that contain these compounds have reached some of the sampled wells. (See p. 42–45.)

CONCLUSIONS

- The frequent detection of VOCs in public well samples reinforces the critical importance of effective well-head protection programs for public wells and the need to further identify and control sources of VOC contamination in these programs.
- Toxicity testing of VOCs historically has focused on individual compounds, typically without consideration of compound mixtures. NAWQA studies contribute to toxicity studies for VOCs by identifying the most commonly occurring chemical mixtures in samples from drinking-water supply wells.

CONCLUSIONS

- The occurrence of THMs in samples from drinking-water supply wells, especially public wells, is attributed to anthropogenic sources, including most notably the capture of recycled water with a history of chlorination.
- The practice of artificial recharge of chlorinated waters to aquifers may require additional evaluation to understand the concentrations and potential concerns of THMs and other chlorination by-products, especially for those aquifers used for drinking-water supply.