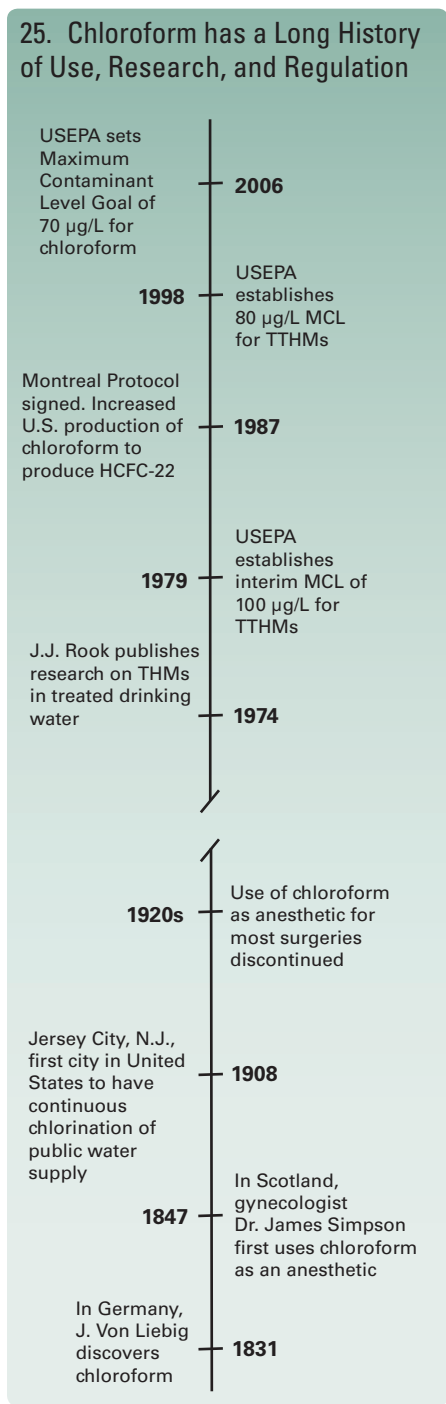


# Chapter 5—Additional Information for Selected VOCs

## Chloroform and Other THMs

### 25. Chloroform has a Long History of Use, Research, and Regulation



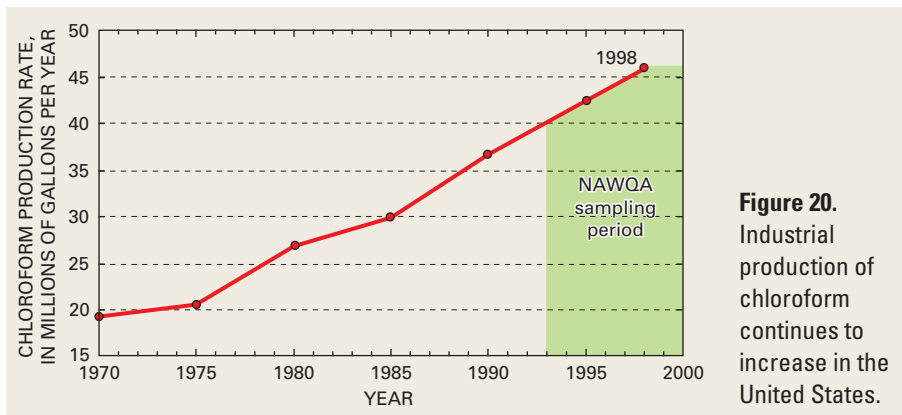
The THM chloroform was the most frequently detected VOC in aquifers (fig. 8), in 7 percent of all samples at an assessment level of 0.2 µg/L. The other three THMs—bromodichloromethane, dibromochloromethane, and bromoform—were each detected in about 1 percent of aquifer samples. Concentrations of chloroform and other THMs generally were less than 1 µg/L. Of samples with detections, the median concentration was 0.08 µg/L for chloroform, and the median **total trihalomethane (TTHM) concentration** was 0.09 µg/L (Appendix 6).

***Chloroform was the most frequently detected VOC in the Nation's aquifers; however, concentrations of chloroform generally were less than 1 µg/L.***

Chloroform has a long history of use, research, and regulation (sidebar 25). In 1999, 98 percent of chloroform produced by industry (fig. 20) was used in the production of the refrigerant hydrochlorofluorocarbon-22 (HCFC-22) to replace dichlorodifluoromethane (CFC-12) for home air conditioners and commercial freezers. The remaining 2 percent of chloroform was used for other purposes, including reagents and extraction solvents,<sup>(59, 60)</sup> fumigants, insecticides, and a precursor for dyes and pesticides.<sup>(61, 62)</sup> In 1998, the most recent year with production data, about 46 million gallons of chloroform were produced by industry.

In contrast to chloroform, the production of the other three THMs has been relatively small; for example, only about 46,000 gallons of bromoform were produced in 1977, the most recent year for which production data are available.<sup>(63)</sup> Furthermore, there is no information on the U.S. production of bromodichloromethane and chlorodibromomethane, presumably because of the limited or non-existent use of these compounds. Examples of limited current or prior use(s) of these three THMs are as solvents for fats, waxes and resins, heavy liquid for geological assays, fire-extinguisher agents, and as an intermediate in chemical synthesis.

Chloroform and other THMs are commonly produced during the chlorination of water and wastewater (sidebar 26). Chlorination of water and wastewater produces an estimated 0.37 million gallons of chloroform in the United States annually,<sup>(64)</sup> which includes the treatment of drinking water, wastewater from municipalities and the bleaching process of pulp and paper, and rinse water from domestic and commercial cleaning and laundry operations. In addition, some THMs occur naturally in the environment (sidebar 27).



**Figure 20.** Industrial production of chloroform continues to increase in the United States.

In studies of the formation of multiple THMs during water chlorination, it has been shown that the relative concentrations (and their relative detection frequencies) usually decrease with increasing bromine content (chloroform > bromodichloromethane > dibromochloromethane > bromoform).<sup>(65,66)</sup> This occurrence pattern also was noted in the NAWQA-collected data,<sup>(11, 13, 36, 67, 68, 69, 70)</sup> and indicates that chlorinated water is an important source of chloroform and other THMs to ground water.<sup>(71)</sup> Sources of chlorinated water to ground water may include irrigation of lawns, gardens, golf courses, and parks; leaking drinking-water distribution and sewer pipes; artificial recharge of wastewater; regulated discharges of cooling process blowdown water from electric power-generating plants; combined sewer overflows;<sup>(62, 72)</sup> and unintended backflow of chlorinated water to supply wells.

***Trihalomethanes (THMs) are produced during water and wastewater treatment when chlorine is added for disinfection.***

Chloroform has been detected in urban air<sup>(73)</sup> and in rainwater.<sup>(74)</sup> In studies of chloroform occurrence in shallow ground water in Indiana<sup>(75)</sup> and New Jersey,<sup>(76)</sup> however, the concentrations of chloroform in the atmosphere and rainwater were not high enough to account for all the mass of chloroform measured in shallow ground water. The sources of the chloroform frequently detected in ground water in the New Jersey study were attributed to use of chlorinated drinking water and the associated recharge from septic tanks or from the irrigation of crops and lawns.<sup>(76)</sup>

Chloroform has been detected in ground water beneath a variety of land-use settings.<sup>(11, 68)</sup> In NAWQA's assessments, THMs were detected more frequently beneath urban residential areas than beneath agricultural areas (fig. 21). Furthermore, the percentage of urban land, the number of RCRA hazardous-waste facilities, and septic system density were shown to be

## 26. THMs Result from Water Chlorination

THMs are a group of VOCs classified as disinfection by-products. THMs in drinking water were first identified by Rook<sup>(77)</sup> and are formed as a result of the haloform reaction when dissolved chlorine combines with dissolved organic matter, such as humic and fulvic acids. The disinfection of drinking water in the United States by chlorination commonly uses chlorine gas, sodium hypochlorite, and calcium hypochlorite. The chemistry associated with the chlorination of water and the formation of chloroform and the brominated THMs are described elsewhere.<sup>(71)</sup> The primary purpose of chlorination of drinking water is to prevent the spread of waterborne diseases, which can include such fatal diseases as cholera and typhoid. Another advantage of chlorination is that a chlorine residual is retained, which provides ongoing disinfection within the distribution system.<sup>(78)</sup> Although the chlorination of drinking water provides many advantages, THMs remain a human-health concern (sidebar 28). Because of this concern, the USEPA has established an MCL of 80 µg/L for the combined concentrations of four THMs (chloroform, bromodichloromethane, dibromochloromethane, and bromoform), also known as TTHMs.

## 27. Some THMs Occur Naturally

Chloroform was originally considered solely of anthropogenic origins; however, several natural sources of chloroform recently have been identified. These include volcanic gases,<sup>(79)</sup> soil fungi,<sup>(64)</sup> and marine algae.<sup>(80, 81)</sup> Although natural sources contribute approximately 90 percent of the total global chloroform flux,<sup>(64)</sup> evidence in the NAWQA-collected data is inconclusive about whether natural sources contribute to chloroform in ground water. Marine algae have been identified as a natural source for bromodichloromethane, dibromochloromethane, and bromoform.<sup>(80)</sup>

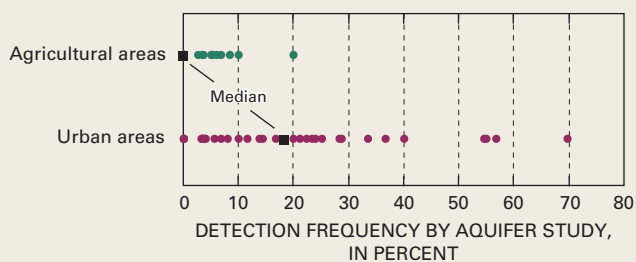
## Chloroform and Other THMs—Continued

### 28. THMs are Associated with Human-Health Problems

THMs are associated with both acute and chronic human-health problems, including nausea, vomiting, dry mouth, dizziness, headaches, and damage to the liver and kidneys with prolonged exposure.<sup>(62)</sup> USEPA Office of Water indicates that three THMs—chloroform, bromodichloromethane, and bromoform—are likely to be carcinogenic to humans. Chloroform, however, is likely to be carcinogenic only at high doses. Chloroform is the only potentially carcinogenic THM for which the more stringent, but not regulatory, MCLG has been raised. Historically, the USEPA has established an MCLG of zero for all carcinogens, including chloroform, based on the presumption that any exposure to carcinogens represents a non-zero health risk. Because chloroform is presumed to be non-carcinogenic to humans at concentrations less than those that cause cell regeneration, the USEPA removed the zero MCLG in May 2000<sup>(62)</sup> and more recently revised the MCLG to 70 µg/L.<sup>(63)</sup> Only one sample from a domestic well and no samples from public wells in this assessment had concentrations greater than the MCLG for chloroform, and no samples had concentrations greater than the MCL for TTHMs.

Recent studies have shown a weak association between the ingestion of THMs and adverse birth outcomes (such as low birth weight, stillbirths, spontaneous abortions, and neural tube defects); however, many of these studies were considered inconclusive. More systematic epidemiological data on reproductive anomalies, including health effects of mixtures of THMs, and better exposure characterization would improve such studies<sup>(64)</sup> and aid regulatory agencies in making informed decisions to further protect human health.

**Figure 21.** Detection frequencies of chloroform in shallow ground water were larger beneath urban areas than beneath agricultural areas.



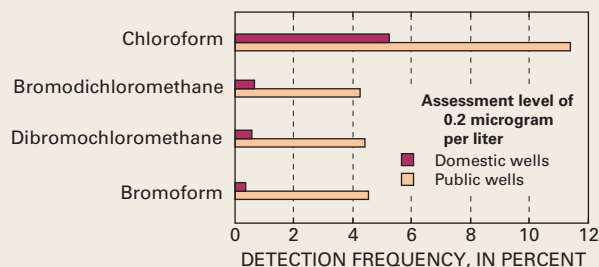
statistically associated with chloroform in aquifers, whereas sewer systems were associated with the occurrence of bromodichloromethane (table 4).

Chloroform was the most frequently detected VOC in samples from domestic and public wells. Detection frequencies of chloroform were about 5 percent in domestic well samples and about 11 percent in public well samples at an assessment level of 0.2 µg/L (fig. 22). As previously mentioned, this difference may be a consequence of the higher pumping rates of public wells and their proximity to developed areas, compared to domestic wells (p. 40 and 41). A pattern of detection frequencies (chloroform > bromodichloromethane > dibromochloromethane > bromoform) is apparent for domestic well samples (fig. 22). This pattern indicates that chlorinated water is an important source of THMs in domestic well water. The frequent occurrence of brominated THMs and THM mixtures in public well samples supports the importance of chlorinated water as a source of THMs to these wells.

***Chlorinated water is an important source of chloroform to ground water.***

Although chloroform was detected frequently, most TTHM concentrations were two orders of magnitude lower than the USEPA MCL of 80 µg/L. No TTHM concentrations in samples from domestic or public wells were

**Figure 22.** Detection frequencies of trihalomethanes (THMs), especially the brominated species, were much greater in public well samples than in domestic well samples.





greater than the MCL (Appendixes 9 and 11). However, each of the four THMs had concentrations less than but within a factor of 10 of the TTHM MCL.

THMs have been detected in septic tank effluent,<sup>(85, 86)</sup> and in improperly designed, maintained, or operated septic systems, resulting in shallow ground-water contamination in the vicinity of the septic system.<sup>(82)</sup> Water from a domestic well may be contaminated if the well is drawing contaminated water from the vicinity of an improperly operating septic system. Other potential sources of chloroform and other THMs to domestic wells are laundry wastewater containing bleach and the well disinfection practice of shock chlorination. In both cases, chloroform and other THMs are produced through the haloform reaction of the chlorine in bleach with organic matter.

***Detection frequencies of THMs were larger in public well samples than in domestic well samples; however, no concentrations were greater than the USEPA drinking-water standard.***

Chloroform and other THMs are persistent under oxic conditions and have relatively low tendencies to sorb to soil and aquifer organic carbon. Because of these properties, THMs are expected to persist and may migrate substantial distances through the subsurface, especially in aquifers with detectable concentrations of dissolved oxygen and low amounts of organic carbon.<sup>(71, 87)</sup> These properties are important considerations in the western United States where drinking-water sources are sparse, and the injection of chlorinated wastewater into aquifers for future supply and to reduce land subsidence may become a more common practice (sidebar 29).

Monitoring chloroform and other THMs in samples from domestic and public wells is important because these compounds likely are indicators of sources of contamination. It also is important to evaluate trends in the occurrence of these compounds and to better understand the origin and human-health relevance of the low concentrations in water supplies.

## 29. THMs Persist in an Aquifer in the Western United States

Chlorinated surface water was injected into an oxic, unconsolidated sand and gravel aquifer in Antelope Valley, California, as part of a program to assess the long-term feasibility of using injection, storage, and recovery as a water-supply method and to reduce water-level declines and land subsidence in Antelope Valley.<sup>(88)</sup> In the sand and gravel aquifer, THM formation continued after the treated water was injected. Once all the residual chlorine reacted, the concentrations of THMs were controlled primarily by mixing and dilution with native ground water. Potential for natural THM attenuation in the aquifer by biodegradation and sorption was low because the aquifer has oxic conditions and low organic matter content.

A model used to forecast the effects of repeated cycles of injection, storage, and recovery indicated that the cycles increased concentrations of THMs in the aquifer. These repeated cycles could yield aquifer THM concentrations approaching 100 percent of the injection-water THM concentration within 10 annual cycles, provided mixing within the aquifer does not lower concentrations markedly.



Trihalomethanes (THMs) in chlorinated irrigation water may reach ground water, especially if recharge occurs. (Photograph courtesy of Rain Bird Corporation.)

## Chlorinated Solvents—Methylene Chloride, PCE, TCA, and TCE

### 30. Production and Use of Chlorinated Solvents have Declined

Chlorinated solvents are used in the aerospace and electronics industries, dry cleaning, manufacture of flexible urethane foam, paint removal/stripping, manufacture of pharmaceuticals, metal cleaning and degreasing, and wood manufacturing.<sup>[91]</sup> Solvents also are present in a variety of household consumer products including drain and pipe cleaners, oven cleaners, shoe polish, household degreasers, deodorizers, leather dyes, photographic supplies, tar remover, waxes, and pesticides.<sup>[92]</sup> Some solvents, such as carbon tetrachloride, have been used as fumigants in grain storage bins.

Production of solvents began in the United States in the early 20<sup>th</sup> century, and usage of solvents increased markedly after World War II. Production has since declined. Nonetheless, relatively large quantities of solvents continue to be used in industrial, commercial, and domestic applications. For example, methylene chloride is an active ingredient in many formulations of paint removers, and PCE is used by more than 80 percent of commercial dry cleaners.<sup>[91]</sup>



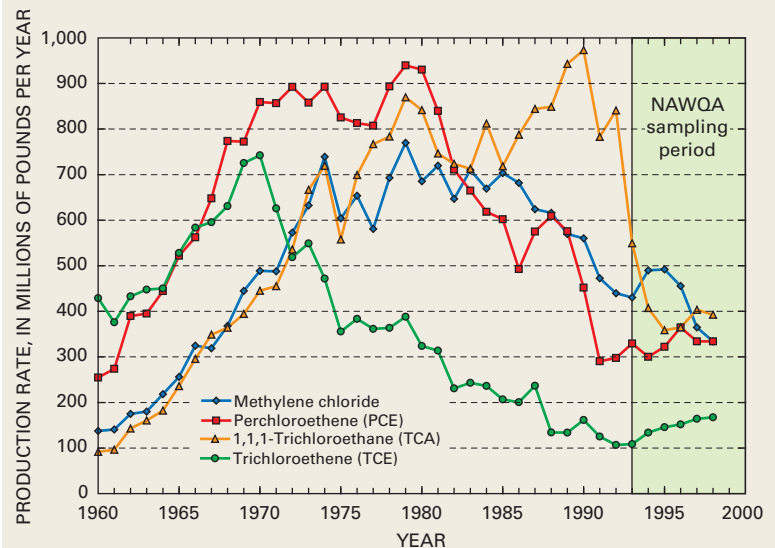
Perchloroethene (PCE) is the most commonly used solvent at commercial dry cleaners. (Photograph by Connie J. Ross, U.S. Geological Survey.)

The solvent group is one of the two most frequently detected VOC groups in the Nation's aquifers (the other is the THM group; fig. 5). Seven solvents were among the 15 most frequently detected VOCs (fig. 8). PCE was the second most frequently detected VOC, and TCE, TCA, and methylene chloride were the 4th, 7th, and 14th most frequently detected VOCs, respectively.

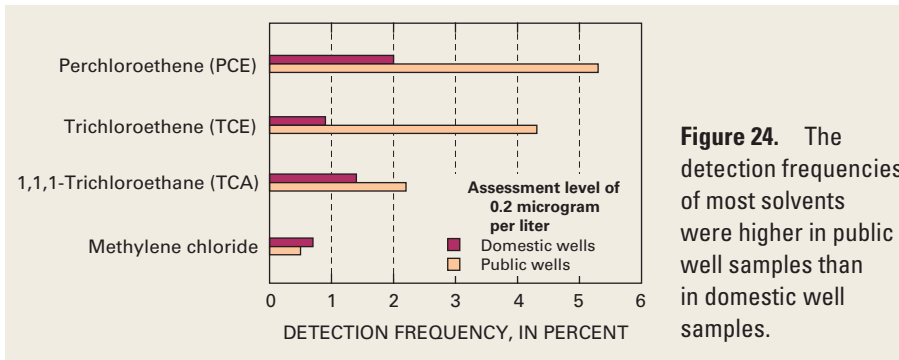
**Seven of the 15 most frequently detected VOCs in aquifers were solvents.**

Chlorinated solvents are organic compounds that are used in a variety of industrial, commercial, and domestic applications (sidebar 30). Four of the most commonly used solvents are given focus here—methylene chloride, PCE, TCA, and TCE. Although relatively large quantities of these solvents are still used today, their production began declining as early as the 1970s (fig. 23) in response to human-health and environmental concerns.<sup>(3)</sup> Specifically, all four solvents have known human-health concerns, and methylene chloride and TCE are classified as **probable human carcinogens** (sidebar 31).

One or more of the four commonly used chlorinated solvents given focus here were detected in about 6 percent of aquifer samples at an assessment level of 0.2  $\mu\text{g/L}$ . Among the four solvents, detection frequencies were about 4 percent for PCE, 3 percent for TCE, 2 percent for TCA, and 1 percent for methylene chloride. The detection frequencies of these solvents,



**Figure 23.** Production of most solvents in the United States began declining as early as the 1970s.<sup>(3, 89, 90)</sup>



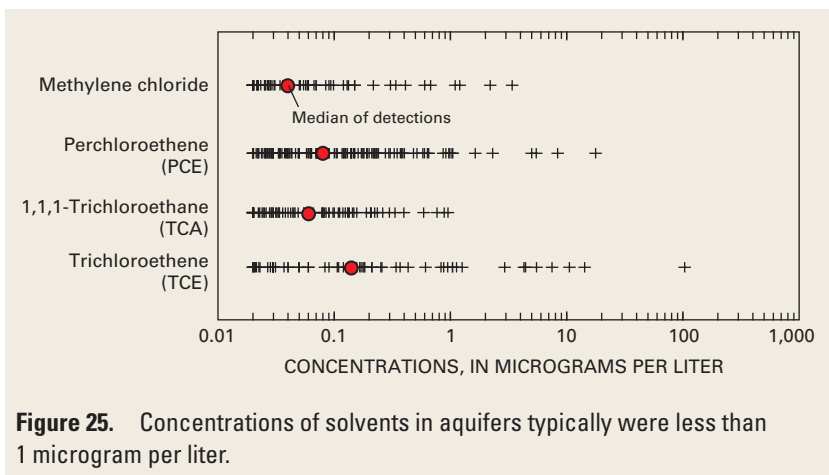
**Figure 24.** The detection frequencies of most solvents were higher in public well samples than in domestic well samples.

except for methylene chloride, were higher in public well samples than in domestic well samples (fig. 24). Solvents also were detected frequently in drinking water supplied by CWSs (sidebar 32).

The **median concentrations of detections** of all four solvents in aquifer samples were less than 0.2 µg/L (fig. 25). TCE had the highest median concentration of detections, followed by PCE, TCA, and methylene chloride. If all laboratory analyses (including non-detections) are considered, the ranking of solvents by concentration is the same as the ranking by detection frequency.

***In samples from domestic and public wells, solvents were among the VOCs that most frequently had concentrations greater than USEPA MCLs.***

In samples from domestic and public wells, the concentrations of 8 VOCs were greater than their MCL, and 3 of these were the solvents PCE, TCE, and methylene chloride. In domestic well samples, TCE and PCE were ranked second and third among VOCs with concentrations that were greater than their MCLs. In public well samples, PCE and TCE were both ranked first, and methylene chloride was ranked third among VOCs with concentrations that were greater than their MCLs. In addition, PCE and TCE had,



**Figure 25.** Concentrations of solvents in aquifers typically were less than 1 microgram per liter.

### 31. Some Solvents are Associated with Human-Health Problems

Chlorinated solvents have been associated with both cancer and non-cancer human-health problems. USEPA Office of Water indicates that both methylene chloride and TCE are probable human carcinogens, although the cancer classification of TCE is under review. TCA is not classifiable for carcinogenicity by the USEPA because of the lack of reported human data and the inadequacy of the available animal studies. The USEPA has not issued any qualitative judgment on the carcinogenicity of PCE.<sup>(83)</sup> The USEPA currently is reassessing the health effects of all four solvents. The final drafts of the reassessments are expected during 2006–2008.<sup>(93)</sup>

MCLs for drinking water (Appendix 9) have been set for all the solvents considered here.<sup>(82)</sup> The potential of solvents to affect drinking water is large, in part, because the water solubilities of the solvents are much greater than their MCLs. This means that even small spills can result in ground-water concentrations of potential human-health concern.



A variety of household products contain chlorinated solvents. (Photograph courtesy of Mike Wolforth, Light Images.)



## Chlorinated Solvents—Continued

### 32. Solvents Occur Frequently in Drinking Water Supplied by CWSs

Drinking water supplied by CWSs sampled during 1993–1998 in 12 New England and Mid-Atlantic States for a previous study had a larger occurrence of solvents compared to samples from domestic wells in the same 12-State area<sup>(70)</sup>. One or more solvents were detected in about 10 percent of samples from CWSs that supply drinking water from ground water and in about 6 percent of domestic well samples. Individual solvents also were detected more frequently in CWS samples than in domestic well samples with the exception of methylene chloride.

Individual solvents were detected much more frequently in large CWSs than in small CWSs. The differences in detection frequencies by CWS size probably are related to larger pumping rates and to more urban land use and higher population density in areas surrounding the supply wells of large CWSs compared to small ones.

In drinking water from CWSs, concentrations of three solvents were greater than MCLs more often than other VOCs. Concentrations of PCE, TCE, and methylene chloride were greater than their MCLs in 1.5 percent, 1.2 percent, and 0.2 percent, respectively, of CWS samples.

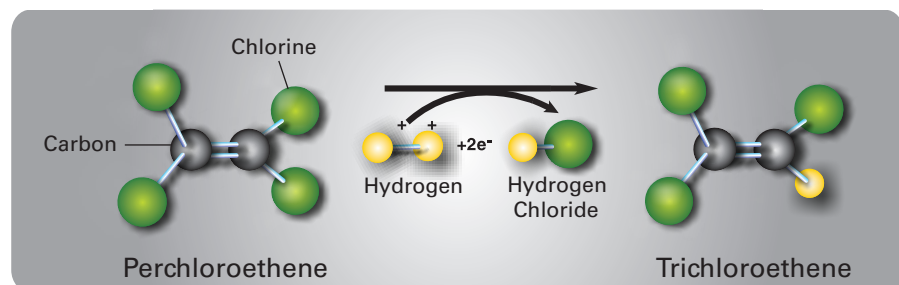
relative to other VOCs, a large number of concentrations less than but within a factor of 10 of their MCLs in samples from public and domestic wells (Appendixes 9 and 11).

The four solvents occurred together in any mixture in 5 percent of aquifer samples at an assessment level of 0.2  $\mu\text{g}/\text{L}$ . The most frequently occurring two-solvent mixture, PCE–TCE, probably represents the degradation of PCE to TCE, which occurs through a process called “**reductive dechlorination**.”<sup>(94)</sup> In reductive dechlorination, a chlorine atom in PCE is replaced by a hydrogen atom producing TCE and is mediated by microbes (fig. 26). Several lines of evidence indicate that at least some PCE is being degraded in aquifers with anoxic conditions (sidebar 33).

***PCE degrades to TCE in aquifers with anoxic conditions.***

A statistical model of solvents in aquifers and shallow ground water indicated that the occurrence of one or more of the four solvents increased with dissolved-oxygen concentrations (table 7). The probability of occurrence of the four solvents also increased with increasing percentage of urban land use, population density, number of RCRA hazardous-waste facilities, and septic system density. Conversely, the probability of occurrence of the four solvents decreased with increasing sand content of soil and depths to the top of the screen/open interval in the well.

The sources of solvents to ground water are numerous and include releases associated with the production, transport, or use of these chemicals. Urban land-use practices, regulated hazardous-waste facilities, and dry-cleaning businesses are likely sources of solvents. Conditions such as recharge, vertical soil permeability, and dissolved oxygen control the transport and fate of the solvents. Although solvents occur in air in urban areas, concentrations are not large enough for atmospheric deposition to account for all the mass of solvents detected in ground water.<sup>(76)</sup>



**Figure 26.** Perchloroethene (PCE) degrades to trichloroethene (TCE) under anoxic conditions through reductive dechlorination.

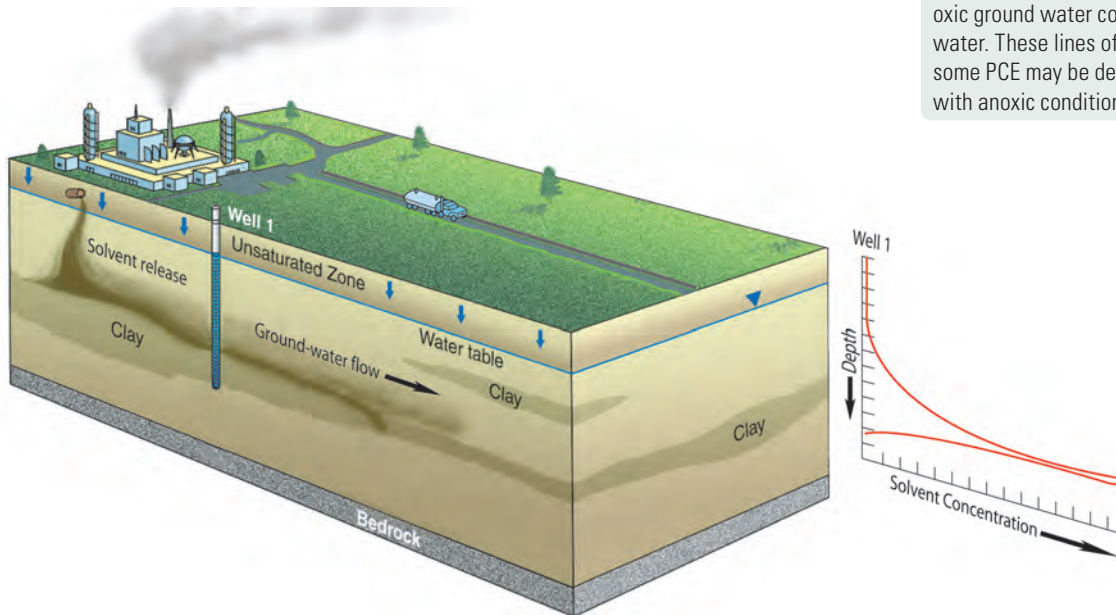
**Table 7.** Explanatory factors associated with the occurrence in ground water of one or more of the four solvents—methylene chloride, perchloroethene (PCE), 1,1,1-trichloroethane (TCA), and trichloroethene (TCE).

[RCRA, Resource Conservation and Recovery Act]

Explanatory factor	Rank	Positive (+) or negative (-) association
Sand content of soil	1	-
Percentage of urban land use	2	+
Dissolved-oxygen concentration	3	+
Population density	4	+
Depth to screen/open interval	5	-
Number of RCRA facilities within 1 kilometer	6	+
Septic system density within 1 kilometer	7	+

***In some cases, concentrations of PCE and TCE increase with depth in an aquifer.***

Because of their physical and chemical properties, different solvents move through and react in ground water in unique ways (sidebar 33). In some cases, the concentrations of PCE and TCE have been shown to increase with increasing depth of the water in the aquifer.<sup>(95)</sup> Because pure solvents are denser than water, they can penetrate the water table and collect in pools on top of less permeable layers in an aquifer. In this way, they become a **source of contamination** at the bottom of the aquifer. Through dissolution, diffusion, and dispersion, the solvent mass can then move upward in an aquifer and produce a concentration gradient that increases with depth (fig. 27).



**Figure 27.** The concentration of a chlorinated solvent may increase with depth in an aquifer.

### 33. What are the Properties of Solvents?

In general, chlorinated solvents, as pure liquids, have relatively high densities, vapor pressures, and solubilities. In ground water, they also have relatively long half-lives. All solvents considered here have densities greater than 1. This means that they are denser than water and that releases of pure solvents can penetrate the water table (fig. 27). The relatively high vapor pressures of the four solvents means that these compounds can volatilize when spilled onto a surface or exposed to the atmosphere. The aqueous solubilities of the four solvents also generally are high.<sup>(96)</sup> Consequently, some mass of solvents exposed to land surfaces can move in solution to the water table. Finally, the biotic half-lives of solvents in ground water are longer than those of other commonly used VOCs, like the gasoline hydrocarbons.<sup>(97)</sup> This means that solvents biodegrade slowly and therefore can persist for long periods of time in certain aquifers.

For more highly chlorinated molecules, the biodegradation of one chlorinated solvent can result in a by-product that also is a chlorinated solvent. For example, PCE can degrade to TCE (fig. 26), especially under anoxic conditions. If this occurs, the detection frequencies and concentrations of PCE should be larger in oxic ground water compared to anoxic ground water. PCE was detected in about 13 percent of samples from oxic ground water, but in only about 6 percent of samples from anoxic ground water. In addition, the concentration ratios of PCE to TCE were three times larger in oxic ground water compared to anoxic ground water. These lines of evidence indicate that some PCE may be degraded to TCE in aquifers with anoxic conditions.

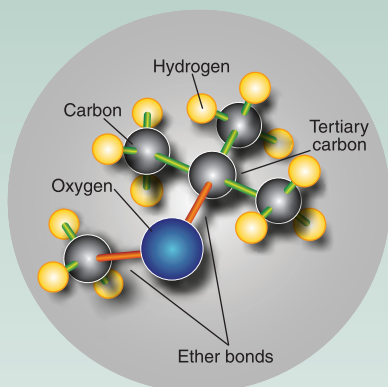


## MTBE and Other Gasoline Oxygenates

### 34. What is MTBE and Why Does it Persist in Ground Water?

MTBE was first introduced in gasoline in 1979 as an octane enhancer resulting from the phase-out of leaded gasoline.<sup>(99)</sup> Since the mid-1990s, MTBE also has been used in large quantities as an oxygenate in reformulated gasoline.

MTBE is an organic compound with ether bonds. The ether bonds and tertiary carbon atom of MTBE make it slow to biodegrade in



ground water.

The physical properties of MTBE include high water solubility compared to gasoline hydrocarbons, low sorption to organic matter in soil and aquifer material, and a tendency to partition from air into water. MTBE also can undergo significant vapor phase transport in the unsaturated zone.<sup>(100, 101, 102)</sup> Collectively, these properties can allow MTBE to reach ground water and to travel faster and farther than other common gasoline components.

In ground water, MTBE is slow to biodegrade.<sup>(102, 103)</sup> MTBE is much less biodegradable than the hydrocarbons benzene, toluene, ethylbenzene, and xylenes (BTEX) in ground water; thus, dissolved MTBE can persist longer in aquifer systems relative to BTEX hydrocarbons.<sup>(104)</sup>

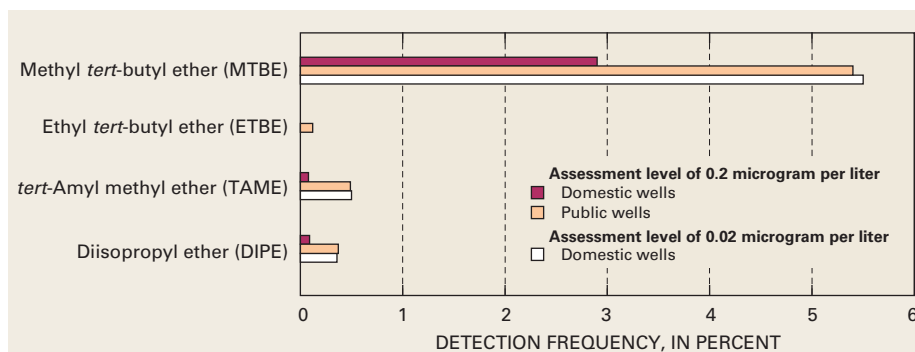
MTBE, a gasoline oxygenate, was the second most frequently detected VOC in samples from domestic and public wells at an assessment level of 0.2 µg/L. The detection frequency of MTBE was about 3 percent in domestic well samples and about 5 percent in public well samples (fig. 28). Public wells generally have larger pumping rates than domestic wells, draw water from larger areas, and thus are more likely to be affected by releases of MTBE. Because of the large overlap in samples between studies of aquifers and domestic wells, the detection frequency of MTBE in aquifers is the same as for domestic well samples.

The NAWQA Program also analyzed samples for three other ether gasoline oxygenates—*tert*-amyl methyl ether (TAME), diisopropyl ether (DIPE), and ethyl *tert*-butyl ether (ETBE). These VOCs were detected infrequently in samples from domestic and public wells (fig. 28).

**MTBE was the second most frequently detected VOC in samples from domestic and public wells despite its relatively short production and use history.**

Gasoline oxygenates are compounds that contain oxygen and are added to gasoline to improve combustion and reduce harmful motor vehicle emissions. Since the 1990s, oxygenates have been used in gasoline in areas where certain air-quality standards have not been attained. In 2004, MTBE was the most commonly used gasoline oxygenate (sidebar 34); however, MTBE has been completely or partially banned in some States (sidebar 35). The Energy Policy Act of 2005 eliminated the oxygen requirement in gasoline.<sup>(98)</sup>

Potential point sources of MTBE include leaking storage tanks and associated piping, tank overflow spills, leaks from transport pipelines or bulk



**Figure 28.** Compared to methyl *tert*-butyl ether, other gasoline oxygenates were detected infrequently in samples from domestic and public wells.

gasoline stations, and automobile and truck accidents. Potential nonpoint sources of MTBE include evaporative losses from tanks or pipelines, incomplete combustion in automobile engines, urban stormwater runoff, exhaust from motorized watercraft, and leaks from watercraft tanks. MTBE has been detected in used motor oil, which also could be a source of MTBE in ground water.<sup>(105)</sup> In some situations, the atmosphere can be a source of MTBE to ground water. This source of MTBE to shallow ground water was studied in a network of sites in southern New Jersey. At some sites, concentrations of MTBE in ambient air and in shallow ground water indicated that the atmosphere was a possible source of MTBE in ground water.<sup>(76)</sup> At other sites, the concentrations of MTBE in ground water indicated that other sources, such as leaking tanks or road runoff, were the dominant source of MTBE.<sup>(106)</sup> In California, artificial recharge in some areas may be a source of MTBE to aquifers (sidebar 36).

Production of MTBE has increased markedly since 1985, with large volumes of MTBE produced in the United States since about 1990 (fig. 29). The locations of ground-water samples analyzed for MTBE, as collected or compiled by the NAWQA Program, and samples where MTBE was detected are shown in figure 30. The locations include samples from studies of aquifers, domestic wells, and public wells. As is evident in this figure, many of the detections of MTBE were in the New England and Mid-Atlantic States.

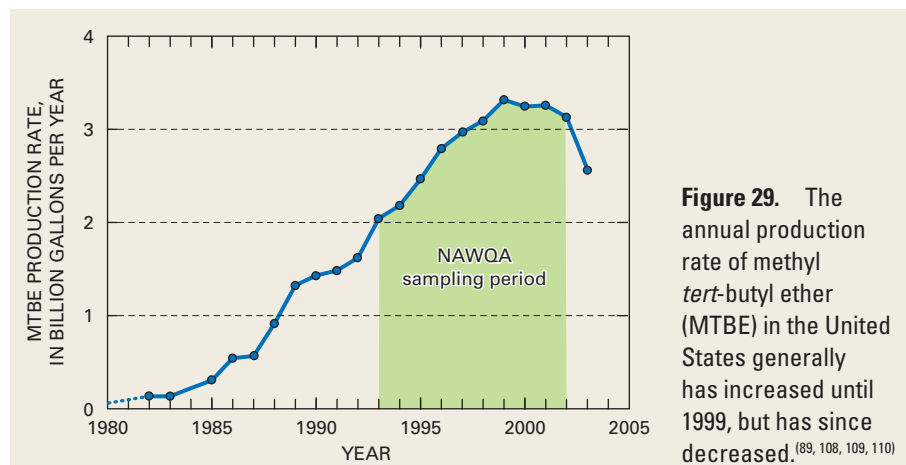
MTBE has been detected in drinking water of some CWSs (sidebar 37). The current concern with MTBE in drinking water is primarily taste and odor because the human-health effects of MTBE have not yet been clearly established. Because of its chemical properties, MTBE can be smelled and tasted at low concentrations by some people. In 1997, the USEPA issued a Drinking-Water Advisory for MTBE.<sup>(107)</sup> The advisory indicates that keeping MTBE concentrations in drinking water below the range of 20 to 40  $\mu\text{g/L}$  will likely avert unpleasant taste and odor effects and also be protective of human health. The USEPA currently (2005) is conducting a risk assessment on the health effects of MTBE.

### 35. MTBE has been Completely or Partially Banned in Some States

As of June 2004, 19 States had enacted legislation to completely or partially ban MTBE use in gasoline.<sup>(111)</sup> Also, several Federal bills and resolutions have been introduced in Congress that would ban or limit the use of MTBE nationwide. As of 2004, however, none of the Federal legislation to restrict MTBE use had been enacted.

After 1995, most of the gasoline in California contained 2 percent oxygen by weight (11 percent by volume) in order to comply with Federal regulations.<sup>(112)</sup> Because of its favorable blending and transfer characteristics in gasoline, MTBE was used as the oxygenate in gasoline in California to comply with air-quality standards. However, because of concerns about the occurrence of MTBE in water supplies, an Executive Order was issued by the Governor of California in 1999 to ban the use of MTBE in gasoline by the end of 2002. In 2002, implementation of the ban was extended to the end of 2003.<sup>(112)</sup>

In 2005, Congress passed the Energy Policy Act that eliminated the oxygen requirement in gasoline as established by the Clean Air Act Amendments (CAAA) of 1990.<sup>(98)</sup> Application of the elimination of the oxygen requirement in gasoline can begin as of the date of the Act (Aug. 8, 2005) for States that received a waiver under the CAAA. Application of the elimination of the oxygen requirement for any other State can begin 270 days after the date of the Act.<sup>(98)</sup> The elimination of an oxygen requirement is expected to result in less use of oxygenates, such as MTBE, in reformulated gasoline.

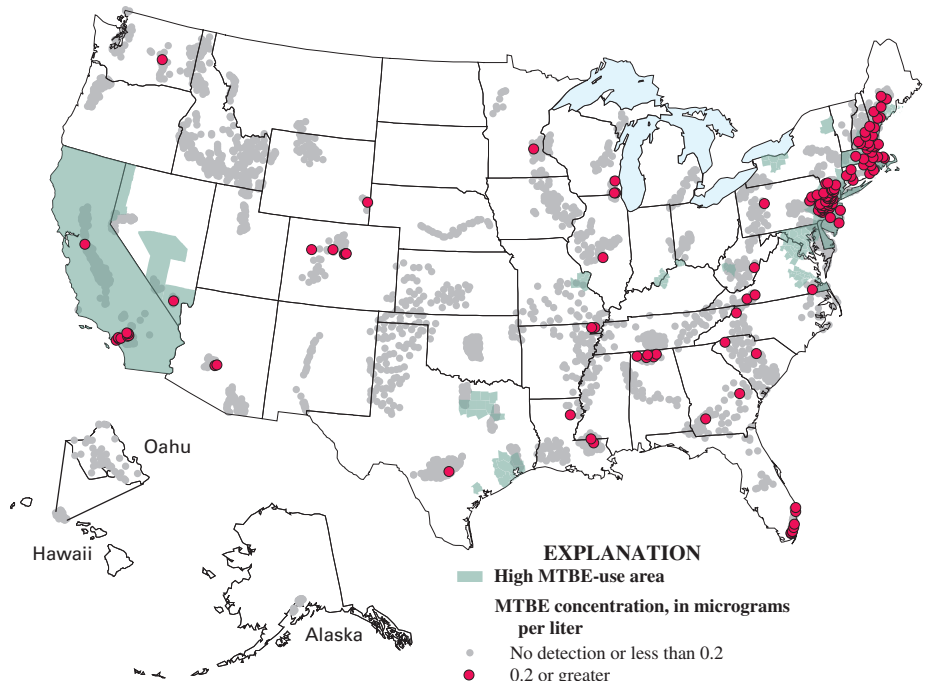


**Figure 29.** The annual production rate of methyl *tert*-butyl ether (MTBE) in the United States generally has increased until 1999, but has since decreased.<sup>(89, 108, 109, 110)</sup>

## MTBE and Other Gasoline Oxygenates—Continued

### 36. Artificial Recharge Areas are a Source of MTBE to Some California Aquifers

In a study of public wells in the Los Angeles Basin (aquifer) and Orange County of southern California, factors such as population density and the density of LUSTs were not associated with the occurrence of VOCs like MTBE.<sup>(114)</sup> This information indicates that localized sources like LUSTs and vertical migration of contaminants are not the dominant factors affecting the occurrence of MTBE in this area. Instead, movement of ground water along flowpaths from artificial recharge areas appeared to be the dominant factor in the occurrence of MTBE in active public wells.<sup>(114)</sup> In general, ground water near the focused recharge areas contained more VOCs like MTBE compared to water farther out in the basins. The occurrence of MTBE close to the areas of recharge is consistent with the relatively recent use of MTBE as a fuel additive and the lateral downgradient flow of recharge water in this area. Further investigation of ground water from public wells in three aquifers in southern California confirmed that MTBE was being introduced into areas of artificial recharge in the aquifers and that concentrations of MTBE decreased along flowpaths in the aquifers.<sup>(115)</sup>



**Figure 30.** Most detections of methyl *tert*-butyl ether (MTBE) are in the highly populated New England and Mid-Atlantic States.<sup>(15, 113)</sup>

Concentrations of MTBE generally were less than the Drinking-Water Advisory, with a median for samples with detections of 0.6  $\mu\text{g/L}$  for samples from both domestic and public wells using an assessment level of 0.2  $\mu\text{g/L}$  (fig. 31). Only one sample from a domestic well had an MTBE concentration that was greater than the lower limit of the Drinking-Water Advisory of 20  $\mu\text{g/L}$ . No samples from public wells had MTBE concentrations greater than 20  $\mu\text{g/L}$ .

***Only one sample from a domestic well and no samples from public wells had MTBE concentrations greater than the USEPA Drinking-Water Advisory.***

In the NAWQA-collected data, the single concentration of MTBE greater than 20  $\mu\text{g/L}$  likely originated from some type of point source.<sup>(113)</sup> Concentrations lower than this level could originate from either point or nonpoint sources. In general, MTBE did not occur frequently with other gasoline components in ground water except when detected at high concentrations.<sup>(113)</sup> The detection of MTBE without other common gasoline hydrocarbons likely is the result of MTBE's higher solubility, lower sorption, and



Smog attributed to motor vehicle emissions was common in many metropolitan areas of the United States prior to the implementation of Federal and State gasoline programs.

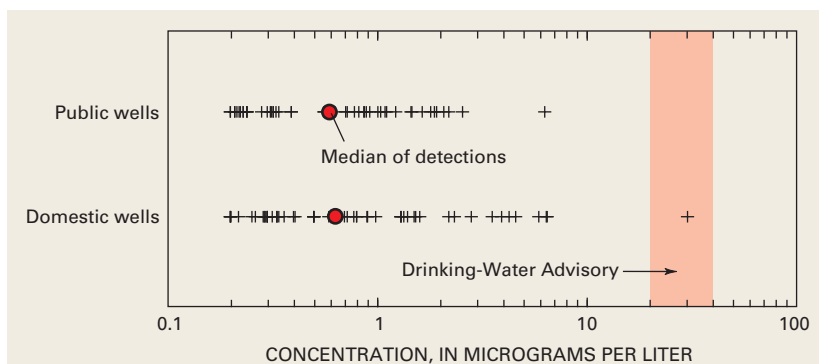
greater persistence in ground water relative to common gasoline hydrocarbons.

In statistical analyses reported previously,<sup>(113)</sup> the probability of detecting MTBE in ground water was greater in areas with high population density, in areas where MTBE is used as an oxygenate in gasoline, and in areas with high ground-water recharge, compared to other areas of the Nation. Public well water and shallow ground water underlying urban land-use areas had a greater probability of containing detectable levels of MTBE than domestic well water and ground water underlying rural land-use areas.<sup>(113)</sup>

When MTBE use in gasoline was applied as a surrogate for MTBE release to the environment, the detection frequency of MTBE was significantly larger in areas of high use than in areas of low use.<sup>(113)</sup> These results indicate that the use of MTBE in large amounts in gasoline in some areas of the Nation has resulted in increased detection frequencies of MTBE in ground water.<sup>(113)</sup> MTBE was detected in some low MTBE-use areas presumably as a result of its small volume in gasoline for octane enhancement.

**Public well water and shallow ground water underlying urban land-use areas had the highest probability of MTBE contamination.**

The quick arrival of MTBE in ground water relative to its production history (fig. 29) indicates that MTBE is an important concern with respect to ground-water management. Aquifers that may be vulnerable to MTBE contamination warrant evaluation with consideration given to the development of strategies to reduce the likelihood of contamination. Continued ground-water monitoring is warranted to evaluate trends in the occurrence of MTBE and to better understand the sources and transport of MTBE to ground water and to domestic and public wells.



**Figure 31.** Most concentrations of methyl *tert*-butyl ether (MTBE) in samples from domestic and public wells are much less than the U.S. Environmental Protection Agency’s Drinking-Water Advisory level.

### 37. MTBE has been Detected in Drinking Water of Some CWSs

MTBE was the fifth most frequently detected VOC in CWS samples collected during 1993–1998 for a previous study in 10 New England and Mid-Atlantic States.<sup>(70)</sup> It was detected in about 9 percent of 985 CWS samples. However, only 0.9 percent of CWSs reported MTBE concentrations greater than 20 µg/L, the lower limit of the USEPA’s Drinking-Water Advisory. Most MTBE concentrations in drinking water were less than 5.0 µg/L.

The USEPA required monitoring of MTBE in drinking water provided by public water systems under the UCM, which was designed to support drinking-water regulations. As of January 2005, 1,859 public water systems with ground-water sources have been sampled for MTBE under the UCM. Only four systems reported MTBE concentrations greater than 20 µg/L.<sup>(116)</sup>



MTBE in drinking water has been a public concern because of its low taste and odor threshold and uncertain human-health effects. (Photograph by Paul J. Squillace, U.S. Geological Survey.)



## Gasoline Hydrocarbons

### 38. Why are Gasoline Hydrocarbons Detected Infrequently in Aquifers?

A variety of physical and chemical properties can limit the movement of gasoline hydrocarbons to and transport by ground water. In ground water, a compound's solubility is one of the most important chemical properties. The median solubility of gasoline hydrocarbons is the lowest of any VOC group.<sup>(118)</sup> Thus, gasoline hydrocarbons have less chance to reach ground water if released because less mass can be dissolved in recharge water.

At a gasoline release site in Beaufort, South Carolina, **aerobic biodegradation** and volatilization were found to be important in limiting the transport and occurrence of gasoline hydrocarbons in the unsaturated zone.<sup>(119)</sup> This could help to explain, in part, the lower detection frequency of gasoline hydrocarbons relative to other VOC groups.

Another important property of organic chemicals is their ability to adsorb to organic carbon in soil and aquifer material. A good measure of the sorption potential is the organic carbon partitioning coefficient. Gasoline hydrocarbons have the highest median organic carbon partitioning coefficient of any other VOC group.<sup>(118)</sup> Because of this, once in the subsurface the movement of gasoline hydrocarbons will be retarded with respect to the velocity of ground water. Also, less mass is left in ground water as sorption occurs.

Finally, and perhaps most importantly, biodegradation can reduce the mass of gasoline hydrocarbons in the unsaturated zone and in ground water. For aerobic biodegradation, gasoline hydrocarbons have some of the shortest half-lives of VOCs (see Circular's Web site). This means that gasoline hydrocarbons biodegrade quickly in oxic ground water relative to other VOCs.

The gasoline hydrocarbon group is defined here as aromatic hydrocarbons or alkyl benzenes whose predominant use is in motor vehicle gasoline. Eleven of the 55 VOCs analyzed by NAWQA are in this group: benzene, *n*-butylbenzene, ethylbenzene, isopropylbenzene, naphthalene, styrene, toluene, 1,2,4-trimethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene.

Gasoline hydrocarbons are among the most intensively and widely used VOCs. Compared to other VOC groups, production of gasoline hydrocarbons has been extremely large. From 1980 to 2000, the median annual production of these compounds for all uses (including motor gasoline) was about 20 trillion gallons.<sup>(117)</sup> This production number was at least four orders of magnitude larger than other VOC groups (sidebar 11) and comprised 99.9 percent of the total production of all VOC groups for the time period.

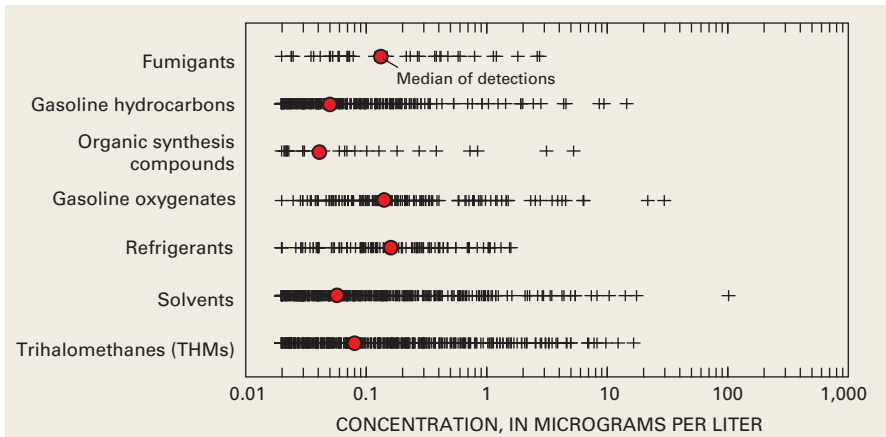
***Gasoline hydrocarbons were detected infrequently in aquifers at an assessment level of 0.2 µg/L.***

Although the production of gasoline hydrocarbons from 1980 to 2000 was substantially larger than that of any other VOC group, it was not the most frequently detected VOC group in aquifers. Both THMs and solvents were detected more frequently than gasoline hydrocarbons at an assessment level of 0.2 µg/L (fig. 5). The smaller detection frequency of gasoline hydrocarbons relative to these other VOC groups probably is attributed to their transport and fate properties (sidebar 38).

Gasoline hydrocarbons were detected most frequently at concentrations less than 0.2 µg/L and comprised a substantial fraction (24 percent) of all low-level VOC detections. The frequent occurrence of low concentrations explains why the median concentration of samples with detections of gasoline hydrocarbons was among the lowest of any VOC group (fig. 32). In drinking water from CWSs, few concentrations of gasoline hydrocarbons were greater than MCLs (sidebar 39).

Individual gasoline hydrocarbons were detected infrequently in aquifers. Only one gasoline hydrocarbon, toluene, was detected in more than 1 percent of aquifer samples (fig. 8). No individual gasoline hydrocarbons were in the top 10 mixtures of VOCs in aquifers (sidebar 13). Furthermore, gasoline hydrocarbons occurred more frequently alone than as mixtures. Two or more gasoline hydrocarbons occurred together in only about 15 percent of samples in which gasoline hydrocarbons were detected.

The sources of most gasoline hydrocarbons in aquifers probably are releases of gasoline or other finished fuel products. However, in addition to their use in gasoline, many of the compounds identified as gasoline hydrocarbons have other uses (Appendix 4) and thus may have other sources to ground water. Gasoline hydrocarbons have been detected in used motor oil, which could be a source for some of these VOCs in ground water.<sup>(105)</sup>



**Figure 32.** The median concentration of gasoline hydrocarbons in aquifer samples with detections was the second lowest of all seven VOC groups.

Because of the infrequent detection of individual gasoline hydrocarbons in aquifers, few associations with anthropogenic or hydrogeologic factors that might control their occurrence could be made in this assessment. The likelihood of detecting either toluene or 1,2,4-trimethylbenzene, however, was determined to be larger in areas with higher density of gasoline storage tanks (table 4).

In a study of the occurrence of MTBE and gasoline hydrocarbons in ground water of the United States, the detection frequencies of individual gasoline hydrocarbons were smaller than the detection frequency of MTBE.<sup>(113)</sup> Although both are components of gasoline, the smaller detection frequencies of gasoline hydrocarbons were believed to be the result of differences in transport and fate properties of these compounds compared to those of MTBE.

***The median concentration of gasoline hydrocarbons was among the lowest of any VOC group.***

In the **Reformulated Gasoline (RFG) Program**, the content of benzene was limited to 1 percent by volume. Normally, gasoline contains between 1 and 1.5 percent benzene by volume.<sup>(120)</sup> RFG usually contains the oxygenate MTBE. The limitation of benzene content in RFG should have resulted in smaller detection frequencies of benzene in areas of high MTBE use compared to areas of low MTBE use. An examination of ground-water data from across the United States revealed that this was the case.<sup>(113)</sup> The smaller detection frequency of benzene, a known human carcinogen, in high MTBE-use areas could be a result of the lower benzene content in RFG and, if so, would be an important change for improving ground-water quality, especially for ground water that is used as a supply for drinking water.

### 39. Gasoline Hydrocarbons Occur More Frequently in Drinking Water from CWSs than in Domestic Wells

Drinking water from CWSs sampled during 1993–1998 for a previous study in 12 New England and Mid-Atlantic States<sup>(70)</sup> had a more frequent occurrence of one or more gasoline hydrocarbons compared to domestic well samples in the same 12-State area. One or more gasoline hydrocarbons were detected in about 8 percent of CWSs deriving drinking water from ground water compared to about 2 percent of domestic well samples. Individual gasoline hydrocarbons also were detected more frequently in CWSs than in domestic well samples, with the exception of isopropylbenzene. The larger detection frequency of gasoline hydrocarbons in CWSs than in domestic well samples is likely due to several factors as discussed previously (p. 40 and 41).

Few concentrations of gasoline hydrocarbons in drinking water from CWSs or in domestic well samples were greater than MCLs. One CWS had a concentration of one gasoline hydrocarbon—benzene—that was greater than its MCL. In domestic well samples from the same 12-State area, no concentrations of gasoline hydrocarbons were greater than MCLs.



More than 1.5 million storage tanks have been removed from service since 1984 to protect soil and ground water from gasoline contamination. (Photograph courtesy of South Dakota Petroleum Release Compensation Fund.)