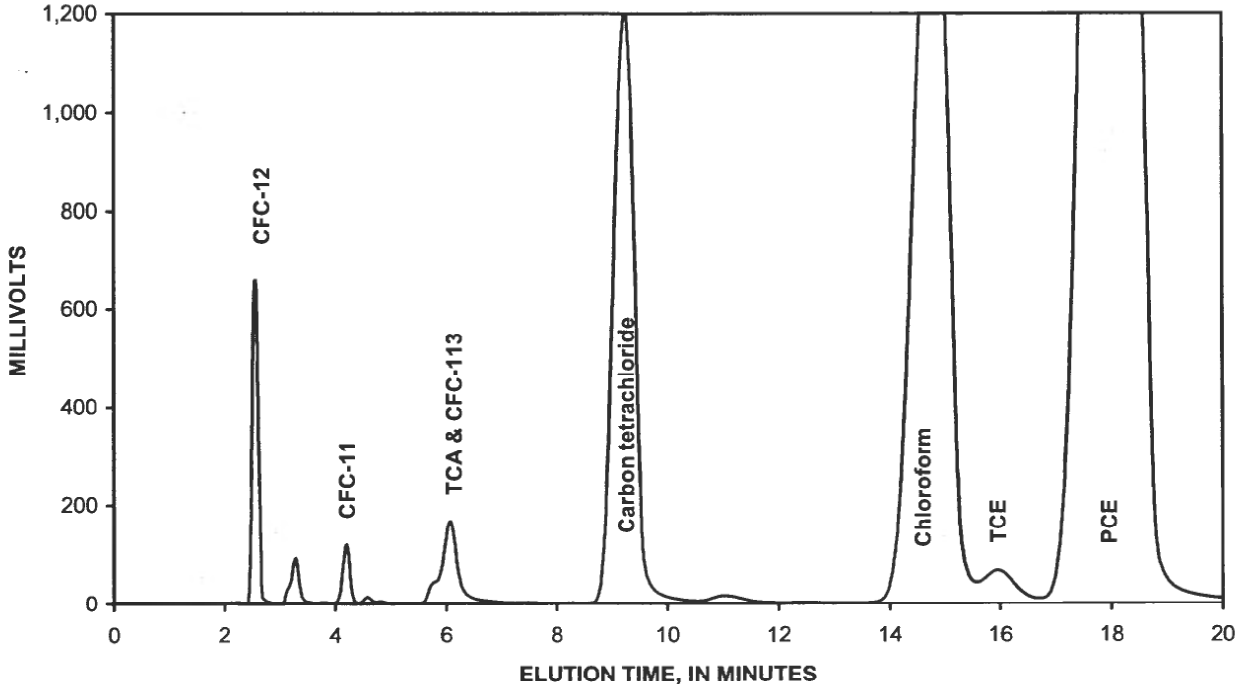
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Occurrence of Volatile Organic Compounds in Drinking Water from the United States: Results from Archived Chromatograms and Water Samples, 1989-2000

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Prepared in cooperation with the U.S. Environmental Protection Agency, Office of Ground Water & Drinking Water



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

Cover graphic: Example of a GC-ECD chromatogram for a sample with numerous VOC peaks from a community-supply well in a fractured-rock aquifer in Virginia.

U.S. Department of the Interior
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By Stephanie Dunkle Shapiro[1], L. Niel Plummer[1], Michael J. Focazio[1], Eurybiades Busenberg[1], Wandee Kirkland[1], and Mario Fernandez Jr.[2]

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Reston, Virginia
2003

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Abbreviations and Acronyms

CCl_4	Carbon tetrachloride
CFC	Chlorofluorocarbon
CFC-11	Trichloromonofluoromethane
CFC-12	Dichlorodifluoromethane
CFC-113	1,1,2-trichloro-1,2,2-trifluoromethane
DCE	1,1-dichloroethylene
GC-ECD	Gas Chromatograph-Electron Capture Detector
GC-MS	Gas Chromatograph-Mass Spectrometer
MTBE	Methyl *tert*-Butyl Ether
NAWQA	National Water-Quality Assessment Program
PCE	Tetrachloroethylene
TCA	1,1,1-trichloroethane
TCE	Trichloroethylene
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
VOC	Volatile Organic Compound
µg/L	Micrograms per liter
pg/kg	Picograms per kilogram

Occurrence of Volatile Organic Compounds in Drinking Water from the United States: Results from Archived Chromatograms and Water Samples, 1989-2000

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ABSTRACT

Archived chromatograms from more than 2,600 untreated ground-water samples representing drinking water collected from throughout the U.S. between 1989 and 2000 were used to assess the occurrence of selected halogenated volatile organic compounds (VOCs). The archived chromatograms were from water samples originally collected for chlorofluorocarbon (CFC) analyses by gas chromatography with an electron capture detector (GC-ECD) by the United States Geological Survey (USGS) Chlorofluorocarbon Laboratory in Reston, Virginia. In addition, 85 archived water samples, which were duplicates remaining from the CFC analyses, were analyzed by gas chromatography in combination with mass spectrometry (GC-MS), to verify the identity of the frequently detected VOCs found on the CFC chromatograms, as well as non-halogenated VOCs that are not detected by the GC-ECD. All samples were flame-sealed in borosilicate ampoules at the sampling site prior to any treatment process, using a consistent protocol that eliminates contact with air.

The six most frequently detected VOCs on the CFC chromatograms include the chlorinated solvents 1,1-dichloroethylene (DCE), 1,1,1-trichloroethane (TCA), carbon tetrachloride (CCl_4), chloroform, trichloroethylene (TCE), and tetrachloroethylene (PCE). These compounds were identified on the basis of a limited number of VOC standards used on the GC-ECD, and were tentatively quantified on the basis of comparisons of peak areas from GC-ECD chromatograms with concentrations from USGS National Water-Quality Assessment (NAWQA) data that were analyzed by GC-MS using purge and trap procedures, and a capillary column.

A total of 91 compounds were identified in the 85 samples analyzed by GC-MS. Eleven of these compounds were identified in 30% or more of the samples, including 1,1,2,3,4,4-hexachloro-1,3-butadiene, 1,2,4-trichlorobenzene, 1,2,4-trimethylbenzene, 1,2-dichlorobenzene, 1,3,5-trimethylbenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, chloroform, m-, p-, and/or o-xylene, PCE, and TCE. These eleven compounds, as well as CCl_4, which was frequently detected by GC-ECD, routinely co-occur in water samples; however, this is likely only the result of their pervasive use and continuous atmospheric presence.

Though the analyses are qualitative, the detection levels for many of the halogenated VOCs were significantly lower (parts per quadrillion) than those of previous studies of drinking water samples in the U.S. due to the use of the GC-ECD in this investigation. For example, CCl_4 was detected in almost every sample analyzed in the USGS Chlorofluorocarbon Laboratory; however, CCl_4 has been infrequently detected in other investigations. In addition to lower detection limits, the data were all obtained with the same collection and analysis procedures, making it a naturally consistent database, unlike many previous national studies that have relied on a combination of data sources. The low-level detections of VOCs in drinking water in this investigation resulted in higher percentages of sites affected by at least trace levels of one or more chlorinated VOC than previously recognized. Seventy percent of the samples contained at least one VOC, and if the CFC data are included, 98% of the samples contained at least one VOC. Most samples analyzed meet United States Environmental Protection Agency (USEPA) drinking-water standards; however, the low-level detections of VOCs can provide a measure of aquifer susceptibility to anthropogenic contamination, and early warning of potential contamination problems.

INTRODUCTION

Approximately 50% of all U.S. citizens, and 97% of U.S. citizens in rural areas, rely on ground water as a source of drinking water (Mlay, 1990). Ground water is susceptible to contamination due to the large number of potential sources of contaminants in contact with or in close proximity to aquifers. Potential contaminant sources across the U.S. include hazardous waste sites, septic systems, surface impoundments, hazardous-waste landfills, municipal and commercial landfills, underground storage tanks, and underground injection wells. In 1984, the USEPA estimated that 75% of the 30,000 to 50,000 hazardous-waste sites across the United States were leaking toxic contaminants into ground water (Lappé, 1991). Countless other sources of potential contamination to ground water include sewage treatment plant outfall, storm water runoff, outfall or dumping from chemical factories, dry-cleaning facilities, application of millions of tons of pesticides and fertilizers to agricultural lands, emissions or spills from motor vehicles as well as refueling stations, and spills or dumping by individual homeowners. All of these potential sources could contaminate ground water with thousands of chemical constituents, of which Federal drinking water standards exist for only a subset.

One group of hazardous substances, referred to as volatile organic compounds (VOCs), is of particular concern to human health. VOCs are among the most toxic environmental pollutants, and many are known or are suspected carcinogens (Lappé, 1991; Thomas, 1990). VOCs generally have low molecular weights, high vapor pressures, and low-to-medium water solubilities (Rathbun, 1998). Because they can aid in the dissolution of many other organic compounds, VOCs are widely used as degreasers, solvents, and cleaning and liquefying agents in fuels, as well as in polishes, cosmetics, drugs, and dry-cleaning solutions. According to Bender and others (1999), VOCs constitute 10 of the top 20 chemical compounds with the largest releases into the environment. Westrick (1990) reports that the ten most frequently identified VOCs include vinyl chloride, 1,2-dichloroethane, 1,2-dichloropropane, DCE, CCl_4, 1,1-dichloroethane, cis/trans-1,2-dichloroethylene, TCA, PCE, and TCE. These ten compounds are chlorinated solvents that are used in many industrial applications as well as in many consumer products. Only 1% are reused or recycled, while the rest are eventually released into the environment, where they are mobile, toxic, and very persistent in soil and water, leading to bioconcentration and ground-water contamination (Harte and others, 1991). In addition, some of these compounds can degrade in the environment into more toxic compounds, such as PCE and TCE, which can degrade to vinyl chloride (Harte and others, 1991).

Attenuation of VOCs in most ground-water flow systems is minimal. Non-destructive processes for the attenuation of VOCs in ground water include evaporation, dispersion and sorption. Numerous destructive processes could work to alter concentrations of VOCs over time in the ground. Reductive dechlorination, which is most efficient under sulfate-reducing or methanogenic conditions, could occur if sufficient organic matter such as aquifer material, major fuel hydrocarbons, or landfill leachate is available (Dinicola and others, 2000). Another process, abiotic degradation, is not typical in normal ground-water environments, and half lives for some chlorinated ethenes by abiotic degradation can be as long as 10^6 to 10^8 years (Jeffers and others, 1989). Mineralization, or direct oxidation, of VOCs occurs under aerobic conditions, and is negligible under methanogenic conditions (Dinicola and others, 2000).

National surveys of VOCs in ground water at the microgram per liter level or lower could provide valuable information to water-resources managers regarding aquifer susceptibility and the potential for concentrations of VOCs to exceed drinking water standards in specific areas. The extent of occurrence in drinking-water supplies from a wide range of VOCs is largely unknown. Large water-supply systems monitor for compounds that are regulated by the USEPA, but typically do not monitor for unregulated compounds. Small water-supply systems and private homeowners are not required to monitor even for regulated compounds. In addition, monitoring for low levels of VOCs provides a database from which research can be conducted on the long-term cumulative and synergistic effects of low concentrations of numerous VOCs on human health and the environment. Little is known about these effects, as research is usually conducted on individual compounds, and regulations are compound-specific.

The USEPA conducted a national survey of VOCs in treated drinking water from ground- and surface-water sources at the 0.2 microgram per liter (μg/L) level from 1975-1981 (Westrick, 1990). This survey documented the occurrence of VOCs in treated

drinking water and focused on the co-occurrence of multiple contaminants, but was unable to assess the quality of the ground-water resource, because VOCs can be added or lost during the treatment and/or distribution processes.

As part of the USGS NAWQA Program, which consists of investigations of surface- and ground-water quality, a national synthesis component to assess the occurrence, sources, and processes affecting VOCs in surface and ground water was added in 1994 (Bender and others, 1999). In the first phase of the NAWQA synthesis, 55 VOCs were included on the basis of which compounds could be analyzed routinely by purge-and-trap gas chromatography/mass spectrometry, and focusing on those compounds that were regulated by the USEPA (Bender and others, 1999). As a subsequent part of the NAWQA synthesis, a retrospective investigation was conducted for 60 VOCs with a minimum reporting level of 0.2-1.0 µg/L in untreated ambient ground water from 2,948 drinking-water and non-drinking-water wells in urban and rural areas between 1985 and 1995 (Squillace and others, 1999). The data for the Squillace and others (1999) investigation were compiled from studies conducted by the USGS and by state, local, and other Federal agencies. Squillace and others (1999) found that five compounds had detection frequencies of 3% or more at the 0.2 µg/L detection limit in drinking-water and non-drinking-water wells in urban and/or rural areas between 1985 and 1995. Westrick (1990) found that five VOCs (*cis*- and/or *trans*-1,2-dichloroethylene, TCA, CCl_4, TCE, and PCE) occurred in water samples from at least 5% of large water-supply systems, while aromatics, especially xylene, had a higher frequency of detection in water from small water-supply systems than in samples from large water-supply systems.

In 1999, the USGS Chlorofluorocarbon Laboratory, located in Reston, Virginia, in cooperation with the U.S. Environmental Protection Agency Office of Ground Water and Drinking Water, began an investigation to assess the presence of low-level detections of VOCs in drinking water utilizing archived chromatograms and water samples that were originally used for measurements of CFC concentrations. The large database from sites sampled and analyzed with consistent protocols from throughout the U.S. between 1989 and 2000, combined with detection levels in the parts per quadrillion range, provides a significant amount of new information for assessing aquifer susceptibility to anthropogenic contamination.

Purpose and Scope

This report provides a retrospective synthesis of VOC data from selected sites that are representative of drinking water sources throughout the U.S. The data were obtained from chromatograms compiled between 1989 and 2000 by the USGS Chlorofluorocarbon Laboratory, as a by-product of CFC analyses, and from archived water samples analyzed during this investigation. Concentrations of CFCs in surface- and ground-water samples from throughout the U.S., as well as in several other countries, have been measured in the USGS Chlorofluorocarbon Laboratory using purge-and-trap GC-ECD since 1989 (see Busenberg and Plummer, 1992; Plummer and Friedman, 1999; http://water.usgs.gov/lab/cfc). Samples come from a wide variety of hydrogeologic and land-use settings, and geochemical conditions. All samples were collected prior to treatment using metal tubing and were fused in borosilicate ampoules without contacting air (Busenberg and Plummer, 1992). Typically, three separate ampoules from each site were analyzed, also without contacting air, and similar results were obtained from all three samples. The CFC analytical detection limit was somewhat variable between samples depending on laboratory and sample conditions, but was typically in the range of 0.3 to 1.0 picograms per kilogram of water (0.3×10^{-12} to 1.0×10^{-12} grams per kilogram, or 0.3 to 1.0 parts per quadrillion). The concentrations can be converted to atmospheric partial pressures and related to historical atmospheric concentrations of CFCs to estimate the year when a water sample was recharged to a ground-water flow system ("apparent recharge year," see, for example, Busenberg and Plummer, 1992; Plummer and Friedman, 1999; Plummer and Busenberg, 2000; http://water.usgs.gov/lab/cfc). Chromatograms from the CFC analyses include information on a variety of other VOCs, and can be used to qualitatively assess low-level occurrences of additional VOCs.

In this investigation, data from chromatograms from previous CFC analyses by GC-ECD are used to identify, and in some cases, tentatively quantify, additional VOCs. In addition to GC-ECD analysis, selected archived water samples were also analyzed by GC-MS. Some of the VOCs identified in this investigation are likely degradation products, as the samples were not acidified or chilled (USEPA requires immediate acidification to a pH of 2, chilling

to 4°C, and analysis within 14 days; Rose and others, 1998). Degradation of CFCs and other VOCs in the archived samples was assessed using GC-ECD analyses of hundreds of water samples stored for as much as 4 years and is typically negligible.

This investigation is based on samples that were originally collected for analysis of CFC concentrations and were not originally intended for identifying other specific VOCs or quantifying other VOC concentrations. Nevertheless, a significant amount of information about numerous VOCs is available from this existing database, because it is an unusually large data set from sites sampled and analyzed with consistent protocols from throughout the U.S. The collection and analysis procedures utilized by the USGS Chlorofluorocarbon Laboratory allow for significantly lower detection limits than previous investigations and eliminate the problem of inconsistent or unknown collection and analysis procedures that have proven problematic in previous retrospective investigations. It should be noted that although CFCs are considered VOCs, throughout this report, the use of the term VOC refers to those VOCs that are not measured quantitatively in the USGS Chlorofluorocarbon Laboratory (those other than CFC-11, CFC-12, and CFC-113).

Acknowledgments

The authors gratefully acknowledge USGS colleagues Gerolamo C. Casile and Julian E. Wayland for CFC analyses, and Sarah E. Parnes for GC-MS analyses. The insightful reviews of the manuscript by James F. Pankow (Oregon Health & Science University, Beaverton, Oregon) and David L. Nelms (USGS, Richmond, Virginia) are greatly appreciated. In addition, the participation of the USGS district office personnel in populating the database for their projects is greatly appreciated.

APPROACH

The VOC data in this investigation are from chromatograms from past CFC analyses and from the analysis of water samples archived until the present investigation in flame-sealed borosilicate ampoules. This section describes the criteria for selecting specific data, and how the data were affected by procedures and conditions in the laboratory over time.

Sample Selection

Wells

Samples collected from ground-water wells or springs in the U.S. were selected for the present study from the USGS Chlorofluorocarbon Laboratory database and sample archive if they were representative of drinking water supplies. The wells or springs either were a direct source of drinking water (community-supply, non-community supply such as for restaurants, and domestic wells) or they tapped aquifers used for drinking water (monitoring, irrigation, and stock wells near drinking-water wells). A total of 2,672 water samples are included in this study, including 2,354 samples from ground-water wells, 317 samples from springs, and one sample from a surface-water site associated with a drinking–water supply (appendix 1). The water samples were collected from 35 states (fig. 1). The largest number of samples was from Virginia (487 samples).

Only samples that fit the above requirements were included. The data are often clustered, and cannot be viewed as a random sampling of drinking-water sites throughout the U.S. because many of the samples were collected as part of large studies to delineate ground-water-flow paths and ages near major public-supply areas, and because samples were included from multiple sampling events over several months or years at specific sites. It should be noted that all samples are considered raw water samples and were collected prior to any chlorination or treatment, thereby eliminating the possibility of formation of trihalomethanes as a result of treatment processes.

Information collected at each site includes, where available, site name and USGS identification number (neither is shown in appendix 1 in the interest of privacy to well owners), state location, county location (not shown), latitude and longitude (not shown), depth of well, length of open interval, land-surface elevation, aquifer name (not shown), water temperature, water level, length of the water column above the open interval, ground-water use, local land use, geochemical conditions during sampling, hydrologic conditions, sampling method, field conditions, materials that contacted the sample, and other ancillary data. Not all information was available at every site. Categories such as ground-water use, local land use, geochemical conditions during sampling, hydrologic conditions, sampling method, field conditions, and materials that contacted the sample were populated using codes

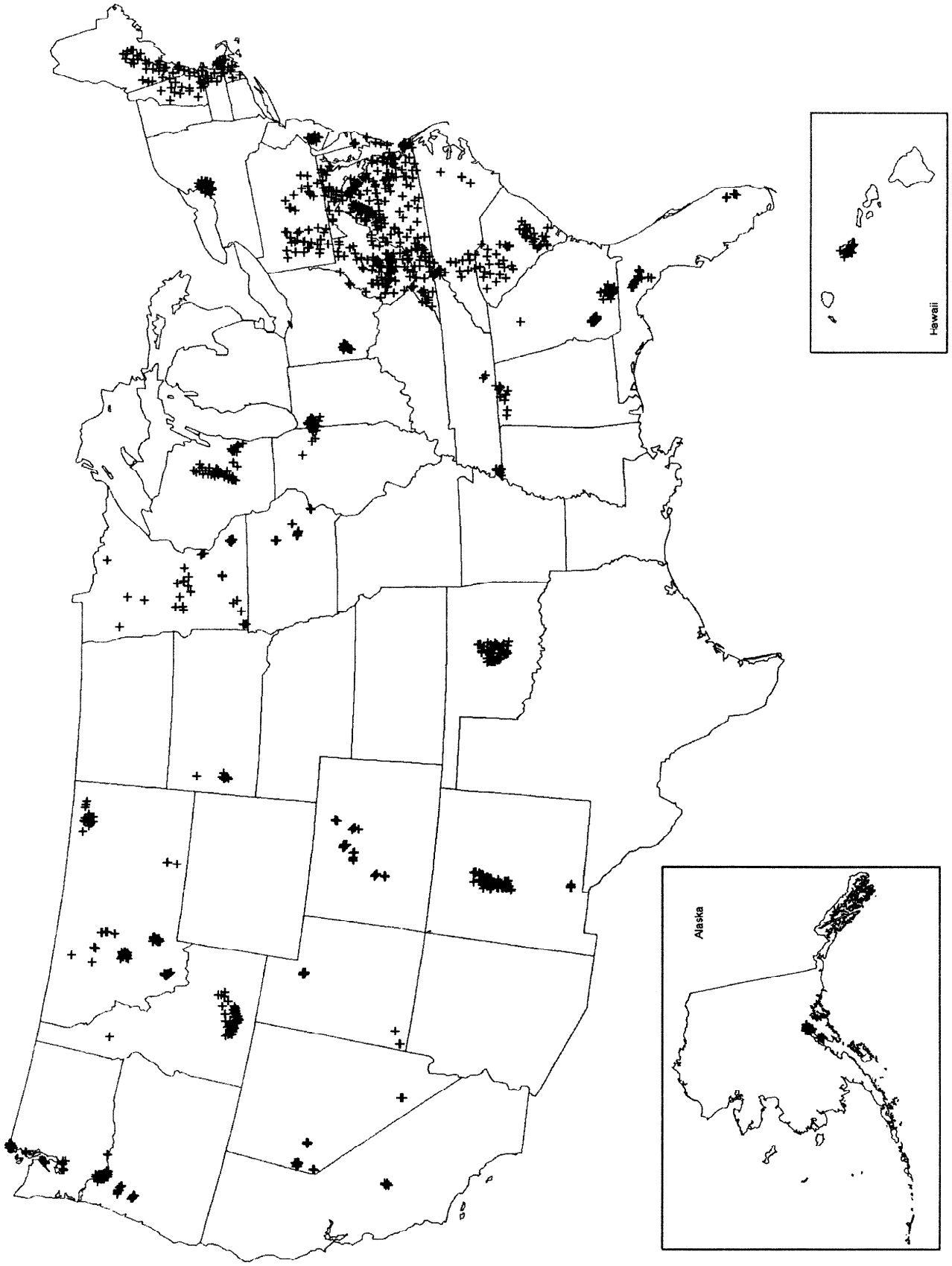


Figure 1. Map of the United Sates showing the locations of sample sites.

developed by the USGS Chlorofluorocarbon Laboratory to aid in the interpretation of CFC concentrations. These codes are shown in appendix 2 and are discussed below.

Chromatograms

The primary objective of this investigation was to tabulate VOC peaks that appear in all archived chromatograms from samples analyzed for CFCs by the USGS Chlorofluorocarbon Laboratory since 1989 that fit the drinking-water criteria described above. Typically, three ampoules were historically analyzed in the USGS Chlorofluorocarbon Laboratory per sampling site; however, only one chromatogram was selected in this investigation for interpretation at each site. This chromatogram was not necessarily the one with the most VOC peaks on the chromatogram, but the one interpreted to be most representative of stable conditions during pumping. For example, the first sample collected at any given site occasionally has higher concentrations of CFCs as well as additional VOC peaks, as a consequence of insufficient purge time or flushing of the sampling apparatus.

Limitations

The CFC analyses conducted by the USGS Chlorofluorocarbon Laboratory were designed to provide picogram per liter detections of CFCs for the purpose of determining modeled recharge dates and ages, but were not designed to give optimum results in determining additional VOCs. Three major analytical issues that significantly affect this investigation include (1) the length of the analysis, (2) the instrument conditions, and (3) the specific GC-ECD instrument that was used for the analyses. These three limitations are detailed below; however, even with the three major limitations in analytical procedures, a large amount of information can be extracted from these data that is relevant to VOC occurrence in drinking water throughout the U.S.

Length of Analysis Time

From 1989 through mid 1992, CFC-113 was not measured, and analyses were conducted for only about 6-8 minutes, therefore eliminating the chance of finding additional VOC peaks with elution times greater than 6-8 minutes (Busenberg and Plummer, 1992; http://water.usgs.gov/lab/cfc). Over the years, the analysis time has been increased to about 20 minutes, and additional VOC peaks have routinely appeared in the chromatograms. In compiling the data for this investigation, the samples with short analysis times appear to have fewer VOC peaks compared to the samples with long analysis times, when in fact they may have had numerous peaks with late elution times. The effect of the analysis time increasing over the years of operation of the USGS Chlorofluorocarbon Laboratory is that the percentage of sites with 0 peaks decreases as analysis time increases (79% for 6-8 minute analyses versus 13% for 18-20 minute analyses) and the total number of peaks measured increases as the analysis time increases (0% with 10 peaks for 6-8 minute analyses versus 0.2% with 10 peaks for 18-20 minute analyses).

Analysis Conditions

There are numerous conditions in the GC-ECD that can vary over time and affect the elution times of the measured compounds. These conditions include variations in the composition and/or quality of the material used to separate the compounds of interest, in the flow rate of the gas used in the system, or in the temperature of the oven (Busenberg and Plummer, 1992; http://water.usgs.gov/lab/cfc). These effects and others can alter the elution times of the compounds on the chromatograms; however, the identity of the predominant compounds remains certain, and the relative elution times remain nearly unchanged for specific compounds.

It should be noted that the CFC data remain quantitative throughout any changes in the USGS Chlorofluorocarbon Laboratory; however, because the GC-ECD used in the USGS Chlorofluorocarbon Laboratory is not designed for the quantitative analysis of other VOCs, the peak areas for the other VOCs are not meaningful. Changes in the oven temperature, in the length of time each VOC is trapped, or in how much of a VOC is being back-flushed, can significantly affect how much of a given compound, particularly those with late elution times, is moving into the detector. Only peaks with areas greater than approximately 100,000 counts are included. Using this threshold, the number of peaks is limited, because it is typical to get just a few counts to tens of thousands of counts on many compounds.

It should also be noted that when peaks for individual VOCs become large, two or more peaks sometimes combine into one very large peak with an elution time between the times that the two individual peaks would have had alone. In such cases, it would appear that there are fewer peaks than are really

present. This situation will be addressed in more detail in subsequent sections. Finally, it should be noted that the VOC peak areas are affected by variations in the headspace in the ampoule. A correction for this is made when determining CFC concentrations, however, the peak areas for individual VOCs are not corrected. The effect of the headspace variation depends on the Henry's law constant of a specific compound and is typically negligible, but the VOCs have not been quantified in this investigation anyway, and the relative peak areas are still meaningful.

Gas Chromatograph

The majority of the CFC analyses were conducted on one instrument that has been in use since 1989 (GC-1). A second instrument (GC-2), added in 1996, was designed to optimize efficiency, and VOCs with elution times that are greater than those of the CFC compounds of interest are flushed out of the system after the CFC compounds have passed into the analytical column. Except for those compounds with exceedingly high concentrations, most of the VOCs are lost from the system. Comparisons of samples from the same site run on both GCs show that samples analyzed on GC-2 had fewer extra VOC peaks and lower peak areas than samples run on GC-1. GC-2 had a larger percentage of samples (79%) with 0 and 1 peak as compared to GC-1 (56%), and a smaller percentage of samples (7%) with more than 2 peaks as compared to GC-1 (28%).

IDENTIFICATION AND QUANTIFICATION OF VOC PEAKS IN GC-ECD CHROMATOGRAMS

In this section, the VOC peaks from the archived CFC chromatograms analyzed by GC-ECD are identified and tentatively quantified on the basis of a limited number of standards analyzed on the GC-ECD, and by comparisons to VOC concentrations from the same wells as determined by USGS NAWQA investigations (John Zogorski, U.S. Geological Survey, written communication, 2001).

GC-ECD Chromatograms

The VOC peaks (other than CFC-11, CFC-12, and CFC-113) from all CFC chromatograms analyzed since 1989 are shown in figure 2 and are tabulated in appendix 3. It is difficult to specify that a peak appearing on a CFC chromatogram is a particular compound due to the lack of standards used for specific VOCs and to variations in the conditions of the instrument over time. However, several groupings of peaks are evident and were identified on the basis of a limited number of VOC standards analyzed by GC-ECD.

Referring again to figure 2, the group with an elution time just before 6 minutes is DCE, followed by TCA just after 6 minutes, CCl_4 around 9-10 minutes (the cluster just after 10 minutes is still CCl_4 from analyses in 1994), chloroform around 14 minutes, TCE just after 15 minutes, and PCE around 18 minutes. In this investigation, CCl_4 was detected most frequently, followed by chloroform, which is primarily because of the high sensitivity of the GC-ECD to these compounds. The ECD is as much as five orders of magnitude more sensitive to CCl_4, for example, than it is to various other VOCs (Devaux and Guiochon, 1967).

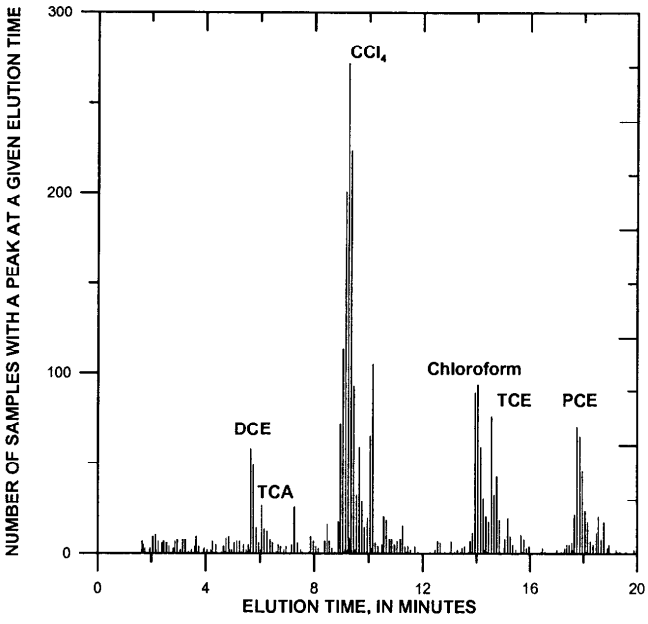


Figure 2. Number of samples that had a VOC peak (other than CFC-11, C, CFC-12, and CFC-113) at a given elution time.

Three of the six primary compounds that appear on the CFC chromatograms included in this study (TCA, TCE, and PCE) are in the top four chlorinated solvents with the highest demand (Harte and others, 1991), which indicates that, as expected, the compounds with the highest demand, or most uses, are the most pervasive contaminants. The VOCs most commonly determined in this investigation are the same compounds that have been identified as those most frequently detected in many previous drinking-water investigations (Grady and Casey, 2001; Moran and others, 2001; Rowe and others, 2001; Squillace and others, 1999; Westrick, 1990; and Zogorski and others, 2001). It should be noted that one peak found in a small percentage of samples is likely N_2O, and not a VOC. This peak was still included if the area was greater than 100,000 because numerous VOC peaks can appear in the chromatograms around this peak, and due to changes in the elution time, it cannot be said with certainty that this peak is always N_2O. The percentage of sites that had this peak was not significant, and including or excluding this peak does not alter the conclusions made in this investigation.

Utilizing all of the VOC peaks detected by the GC-ECD, 70% of the samples contained at least one VOC. This value increases to 98% if the CFC data are included. These percentages should be viewed as minimum estimates because the entire data set was utilized, and as discussed previously, only peaks with areas greater than 100,000 counts were included, some of the samples were only analyzed for six to eight minutes, and many of the samples were analyzed on GC-2.

Comparison of GC-ECD VOC Peaks with VOC Concentrations from NAWQA Investigations

For 124 of the sites from this study, a comparison was made between CFCs concentrations and VOC peak areas detected in this investigation (by GC-ECD) and CFC and VOC concentrations from USGS NAWQA investigations (appendix 4; John Zogorski, written communication, 2001). This comparison is useful in order to determine the concentration ranges for VOCs identified as a by-product of CFC analyses. Data for the samples from NAWQA investigations were obtained using purge-and-trap GC-MS with a capillary column. For 99 of these sites, the sampling for the NAWQA investigations was done on the same day as the sampling for CFC analyses by the USGS Chlorofluorocarbon Laboratory. For the remaining sites, the offset between sampling events is from 3 to 353 days (a cut-off of one year was chosen to minimize hydrologic differences).

For the CFCs, the concentrations determined in this investigation using the GC-ECD are as much as five orders of magnitude lower than the minimum reporting level for the samples analyzed in the NAWQA studies. For example, CFC-11 and/or CFC-12 concentrations are reported for only 12 NAWQA samples (appendix 4). In all other samples, the concentrations reported from NAWQA investigations were below the minimum reporting level. For these twelve samples, however, concentrations determined in the USGS Chlorofluorocarbon Laboratory were as much as two orders of magnitude above the calibration range of the GC-ECD, and all except one are reported in appendix 4 with either a '>' symbol indicating that the concentration is likely higher, but was too far above the calibration range to be determined more accurately, or were reported as 'NA,' because in these cases, the concentration was so far above the calibration range of the instrument that even a relative number could not be assigned. For example, in this investigation, site 2614 had a CFC-12 concentration of >71,100 pg/kg, which is more than an order of magnitude above the calibration range for the USGS Chlorofluorocarbon Laboratory. The concentration reported from a NAWQA study for this site is 1.04 µg/L, or 1,040,000 pg/kg. This discrepancy occurs for the other CFC concentrations reported in NAWQA investigations; however, the lowest detectable concentrations reported in various NAWQA investigations correlate with the highest concentrations measured in the USGS Chlorofluorocarbon Laboratory. The difference in the detection levels between the USGS Chlorofluorocarbon Laboratory and the NAWQA investigations results from the different sampling and analysis methods used by the two groups. Samples collected for CFC analysis at the USGS Chlorofluorocarbon Laboratory were collected using metal tubing and fused in borosilicate ampoules without contacting air. Samples were analyzed using GC-ECD methods again without contacting air, thereby eliminating any chance of atmospheric exchange and allowing the detection of VOCs at levels that are below modern atmospheric air-water equilibrium (Busenberg and Plummer, 1992).

A comparison was made of concentrations of DCE measured in NAWQA studies and peak areas from the GC-ECD chromatograms; the DCE peak appears just before CFC-113 and is not back-flushed or lost during the GC-ECD analysis. Of all the VOC peaks (other than CFC-11, CFC-12, and CFC-113) identified conclusively in this investigation, the DCE peak is the most quantitative. The peak areas from the CFC chromatograms increase linearly as the concentration reported from NAWQA studies increases (fig. 3). Using this correlation, concentrations for numerous samples with smaller peak areas than those used to make the correlation can be estimated and are in the range of 0 to 0.008 ug/L (fig. 3).

Direct comparisons between VOC peaks (other than CFC-11, CFC-12, and CFC-113, and DCE) in this investigation and those from the NAWQA studies are difficult for several reasons. For example, not all of the 124 sites for which there is overlap between data from this investigation and data from the NAWQA studies were analyzed for 20 minutes, in which case peaks with late elution times would not appear. In numerous cases, chloroform and/or PCE are reported in NAWQA studies, when due to insufficient run time, no peaks are reported for chloroform or PCE from the GC-ECD chromatograms (appendix 4). For samples with high concentrations of any VOC, other VOCs can be masked on the GC-ECD chromatograms by the large peaks and do not appear to be present. For example, if CFC-113 is high, TCA can be masked. If concentrations of chloroform, TCE and/or PCE are high, they can combine into one large peak with an elution time that is shifted to the mid-point of the combined peak (for example, for site 1644, for which NAWQA investigations detected chloroform (1.8 µg/L), TCE (3.957 µg/L), and PCE (0.1639 µg/L), all three peaks on the chromatogram are merged, and the detector labels two at 13.92 and 17.65 minutes, instead of three at ~14, 15, and 18 minutes). Also, if the concentration of a VOC is high enough, the detector becomes saturated and no other peaks are seen (for example, site 413, for which NAWQA investigations detected chloroform (0.1122 µg/L), TCE (20.44 µg/L), and PCE (0.3556 µg/L), and the chromatogram shows that the detector is 'saturated' after 13 minutes). It is generally possible to assess if there is more than one compound present in the GC-ECD chromatogram, especially if multiple

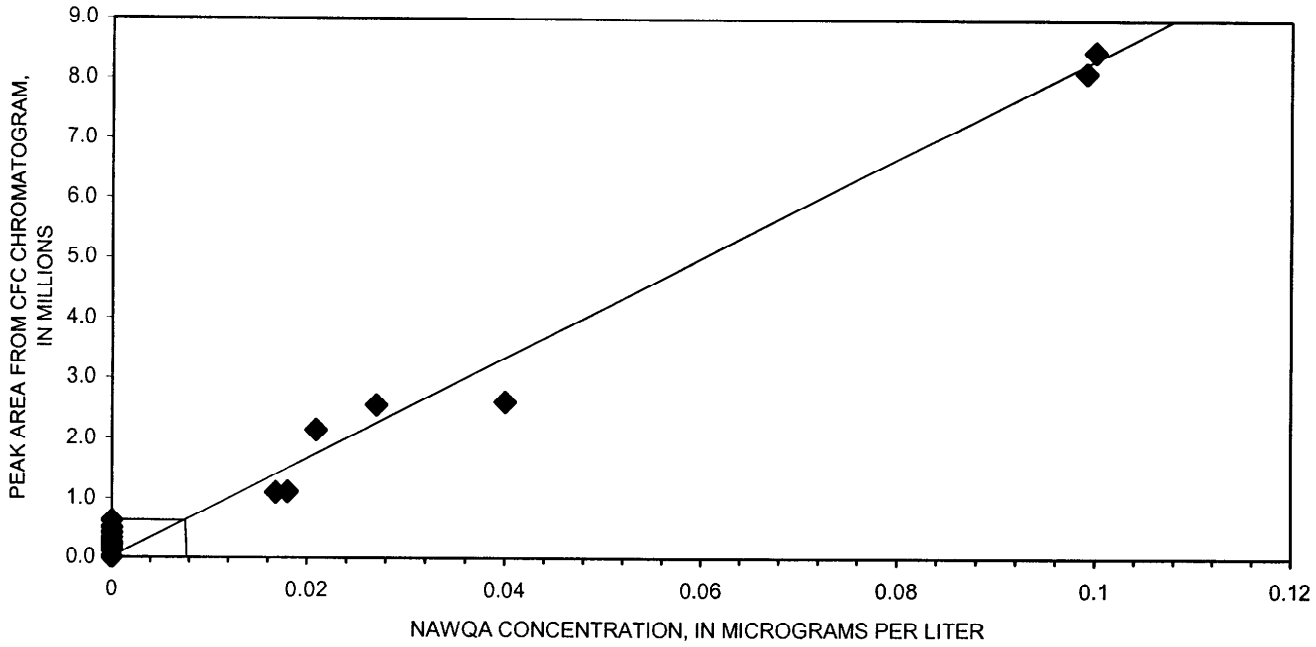


Figure 3. GC-ECD peak areas versus concentrations from NAWQA investigations for 1,1-dichloroethylene.

ampoules are analyzed; however, this cannot be done with certainty.

Individual peaks can be separated when the concentrations are small. For example, for site 1005, the USGS Chlorofluorocarbon Laboratory detects individual peaks for TCE and PCE that have NAWQA-reported concentrations of 0.0094 µg/L, and 0.048 µg/L, respectively. For site 2593, the USGS Chlorofluorocarbon Laboratory detects individual peaks for chloroform, TCE, and PCE, for NAWQA-reported concentrations of 0.04 µg/L, 0.006 µg/L, and 0.123 µg/L, respectively. The GC-ECD peaks for the lowest reported concentrations for chloroform, TCE, and PCE are hundreds of thousands of counts, millions of counts, and tens of millions of counts, respectively. The GC-ECD appears to be most useful for chloroform, TCE, and PCE concentrations below about 0.04, 0.01, and 0.05 ug/L, respectively. Carbon tetrachloride is detected in almost every sample analyzed in the USGS Chlorofluorocarbon Laboratory; however, in NAWQA investigations, CCl_4 is detected in only five samples (as low as ~0.1 µg/L). For the lowest concentrations reported from NAWQA investigations for CCl_4, the GC-ECD peaks are so large that peak areas cannot be assigned. The discrepancy between the laboratories for the detection of CCl_4 is a function of the sensitivity of the GC-ECD to CCl_4 as discussed above.

IDENTIFICATION AND QUANTIFICATION OF VOC PEAKS IN GC-MS CHROMATOGRAMS

A subset of stored samples was selected for analysis by GC-MS. About half of these samples were collected from domestic and community/non-community-supply wells in five states. These wells were sampled in the year 2000 and were selected to minimize any effects from storage in the ampoules. The second set of samples, which were stored in ampoules for up to four years, were selected because they had numerous VOC peaks on the GC-ECD chromatograms. The GC-MS analyses were used to corroborate the identity of the VOCs detected on the GC-ECD, as well as to identify non-halogenated VOCs that are not detected by the GC-ECD.

GC-MS Chromatograms

Archived ampoules from 85 sites were analyzed by GC-MS. A Hewlett Packard (HP) 5973 mass selective detector with a mass range of 34 to 550 atomic mass units was used in combination with an HP 6890 gas chromatograph. The VOCs were preconcentrated using purge and trap procedures, cryofocused, and injected into a 60m x 0.32mm x 1.8µm HP-VOC/MS capillary column. Specific VOCs were tentatively identified, but not quantified, using the National Institute of Standards (NIST) Mass Spectral Library (version 1.6) which has more than 61,000 chemical structures and MS spectra. Specific peaks were considered positively identified if there was a 90% or greater chance that the mass spectrum matched a specific spectrum in the library (appendix 5). These are listed in appendix 5 as GS, GM, or GL depending on whether the peak area was <10,000, 10,000-19,999, or ≥20,000, respectively. In addition, other compounds were tentatively identified and listed if the peak correlated with a peak identified in the standard (appendix 5). These compounds are listed similarly to those positively identified, except that an 'E' was added (GES, GEM, GEL). A total of 91 compounds were identified in the 85 samples analyzed by GC-MS (appendix 5).

In general, if the GC-ECD chromatogram had no peaks other than the CFCs, few peaks were detected by GC-MS (figs. 4 and 5). Figure 4 shows GC-ECD (4a) and GC-MS (4b) chromatograms from an 870-foot deep drinking-water well in Hawaii, completed in an unconfined, fractured-rock aquifer beneath an urban/residential area (Site #408). The water is oxygenated, contains virtually no VOCs, has modeled CFC-11, CFC-12, and CFC-113 recharge years of 1954, 1952, and <1955, respectively, has a low tritium value (0.11 TU), and has an 85-year old ^{3}H-^{3}He modeled age, which is beyond the practical dating range of the method. This water is relatively old and is unaffected by modern anthropogenic inputs. Figure 5 shows GC-ECD (5a) and GC-MS (5b) chromatograms from a 182-foot deep domestic well in Maine, which is completed in a semi-confined, fractured-rock aquifer beneath a residential area (Site #988). The water is methanogenic, contains virtually no VOC peaks, and has modeled CFC-11, CFC-12, and CFC-113 recharge years of <1945, 1964, and <1955, respectively. The concentrations of VOCs in this water may be affected by degradation processes, as is typical under

methanogenic conditions; however, the sample appears to be representative of water that is relatively unaffected by anthropogenic activity.

If the GC-ECD chromatogram had many peaks other than the CFCs, numerous VOCs were also identified by GC-MS (figs. 6 and 7). Figure 6 shows GC-ECD (6a) and GC-MS (6b) chromatograms from a 625-foot deep community-supply well in Virginia that is completed in an unconfined, fractured-rock aquifer beneath an urban area (Site #1992). The water is methanogenic, has numerous VOC peaks, and has a modeled CFC-11 recharge year of 1975, but CFC-12 and CFC-113 concentrations are above modern air-water equilibrium (i.e., contaminated). This well is likely contaminated and the older CFC-11 modeled-age is likely the result of degradation of CFC-11. Figure 7 shows GC-ECD (7a) and GC-MS (7b) chromatograms from a 59-foot deep community-supply well in Virginia, in a discharge area of an unconfined aquifer (Site #1909). The water is oxygenated, contains tens of VOC peaks, has a modeled CFC-11 recharge year of 1988, but CFC-12 and CFC-113 concentrations are above modern air-water equilibrium (i.e., contaminated), and has a fairly high tritium value (9.51 TU). This water has likely been recharged in approximately the last 5 years and has many indicators of anthropogenic inputs.

Eleven compounds were identified in 30% or more of the samples analyzed by GC-MS. These eleven include 1,1,2,3,4,4-hexachloro-1,3-butadiene (77.6%), 1,2,4-trichlorobenzene (74.1%), 1,2,4-trimethyl-benzene (62.4%), 1,2-dichlorobenzene (62.4%), 1,3,5-trimethylbenzene (38.8%), 1,3-dichloro-benzene (62.4%), 1,4-dichlorobenzene (61.2%), chloroform (31.8%), m-, p-, and/or o-xylene (35.3%), PCE (32.9%), and TCE (34.1%). Three of these were also in the six most frequently detected compounds identified using the GC-ECD chromatograms (chloroform, TCE, and PCE). Carbon tetrachloride was the most frequently detected compound on the GC-ECD chromatograms, but was detected in only seven of the GC-MS samples. The sensitivity to CCl_4 of the GC-MS could be increased if the range of the scan for each sample were decreased to focus on the period when CCl_4 would appear.

Comparison of GC-MS VOC Peaks with GC-ECD VOC Peaks and VOC Concentrations from NAWQA Investigations

For 55 of the sites from this study, a comparison was made between CFCs and VOCs detected in this investigation by GC-ECD and by GC-MS, and CFC and VOC concentrations from NAWQA studies (appendix 5). In appendix 5, data from NAWQA investigations are available only for the shaded samples and are reported as N or NE, depending on whether the concentration was actual (above the minimum reporting level) or estimated. The compounds for which there is overlap with all three methods of detection include CCl_4, chloroform, TCA, 1,1-dichloroethane, DCE, PCE, and TCE. This would be expected because these compounds can be detected by all three methods (unlike some of the other compounds listed), and they are among the most commonly used and detected VOCs.

While all three methods can detect numerous compounds, each method appears to be particularly useful for detecting certain compounds. The GC-ECD appears to be most useful in detecting concentrations of CFCs, CCl_4, chloroform, PCE, and TCE in the parts per quadrillion range. The GC-ECD data for VOCs other than CFC-11, CFC-12, and CFC-113 are not quantified, but can be utilized for surveying low-level contamination in aquifers. The GC-MS appears to be most useful in detecting 1,1,2,3,4,4-hexachloro-1,3-butadiene, 1,2,4-trichlorobenzene, 1,2,4-trimethylbenzene, 1,2-dichlorobenzene, 1,3,5-trimethylbenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, and m-, p-, and/or o-xylene. NAWQA investigations routinely provide quantitative measurements of a wide array of the VOCs, but at concentrations typically greater than 0.1 µg/L.

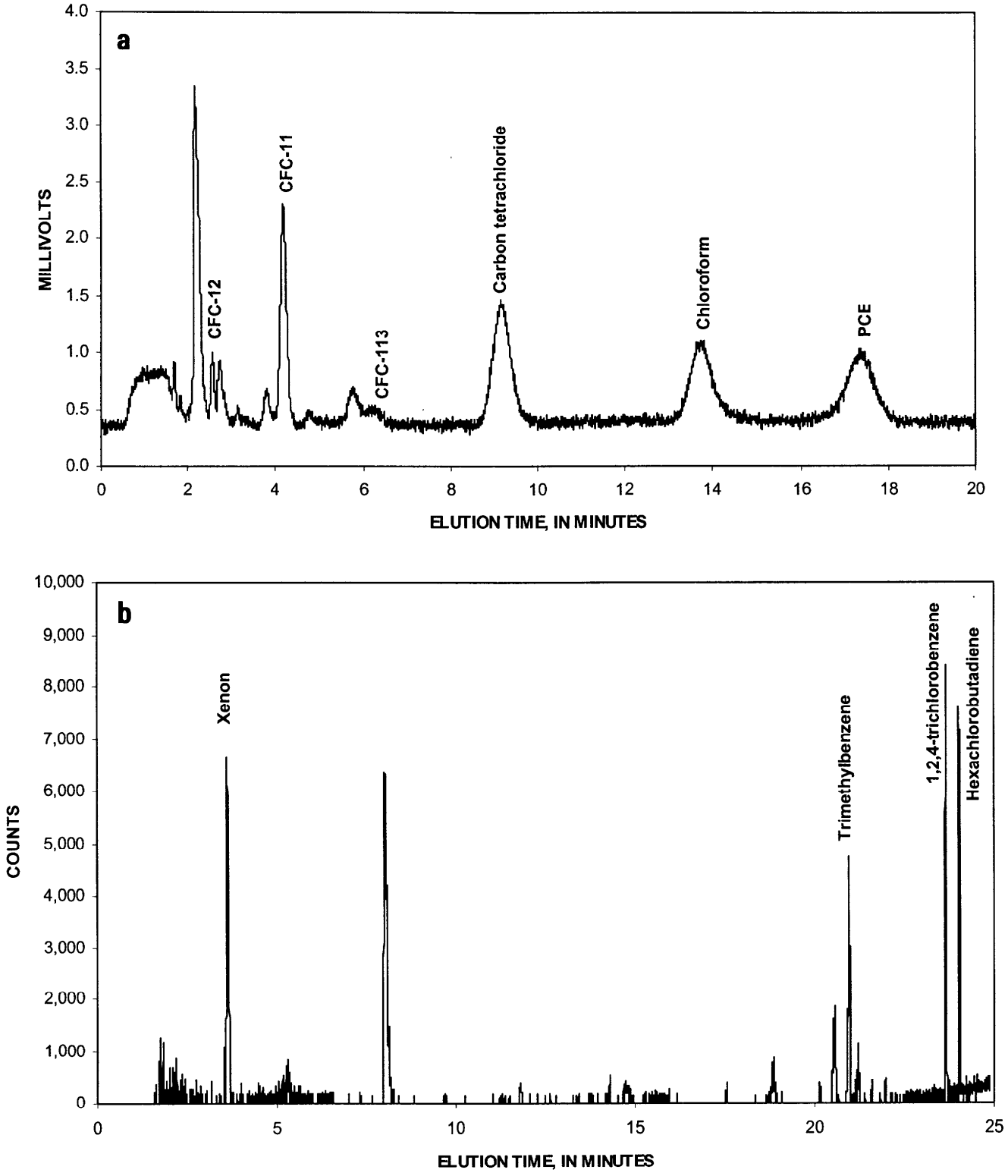


Figure 4. Example of GC-ECD (a) and GC-MS (b) analyses for a sample without many VOC peaks from a non-community supply well in Hawaii. Note scale of y-axis relative to scale of y-axis in figures six and seven.

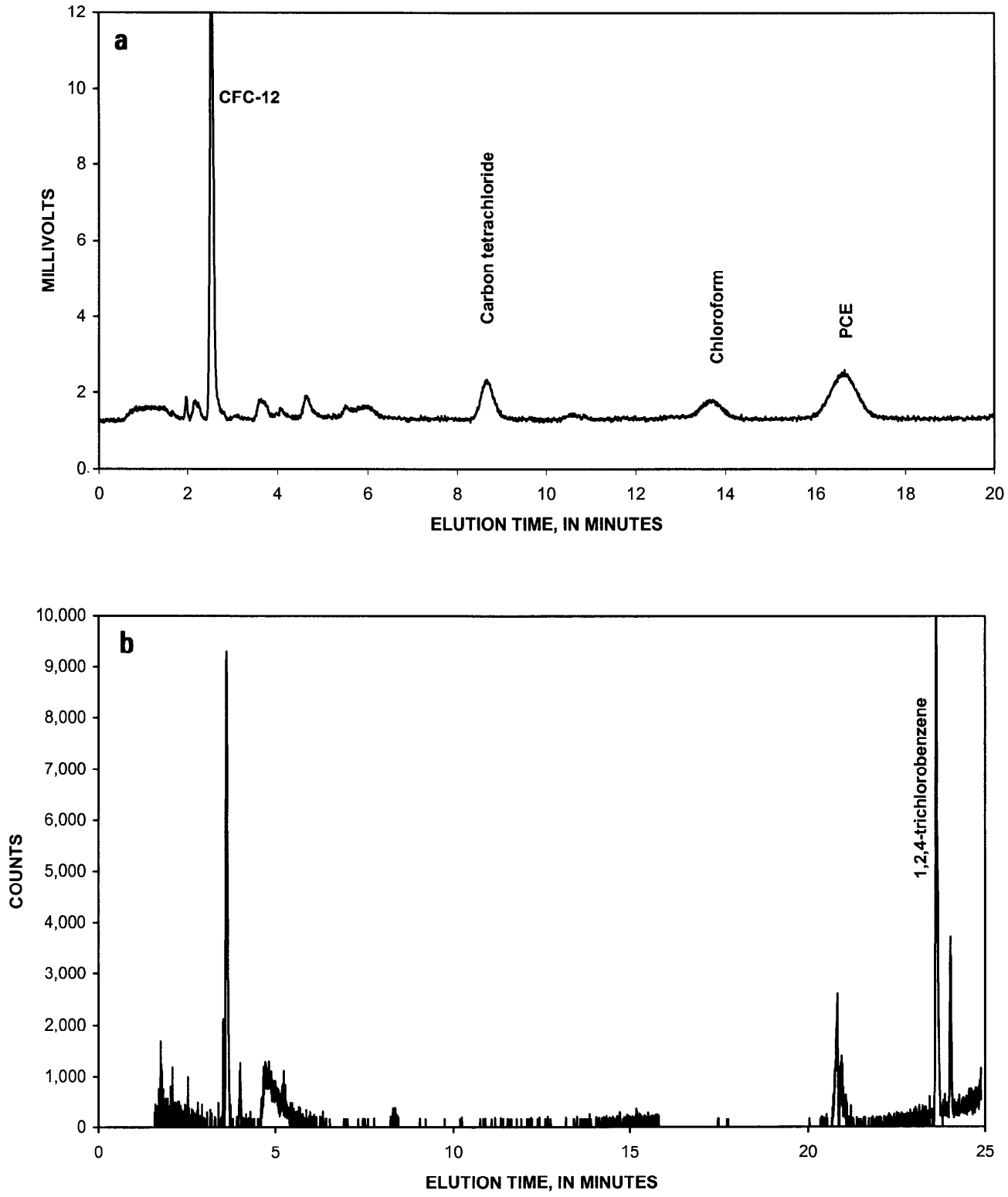


Figure 5. Example of GC-ECD (a) and GC-MS (b) analyses for a sample without many VOC peaks from a domestic well in Maine. Note scale of y-axis relative to scale of y-axis in figures six and seven.

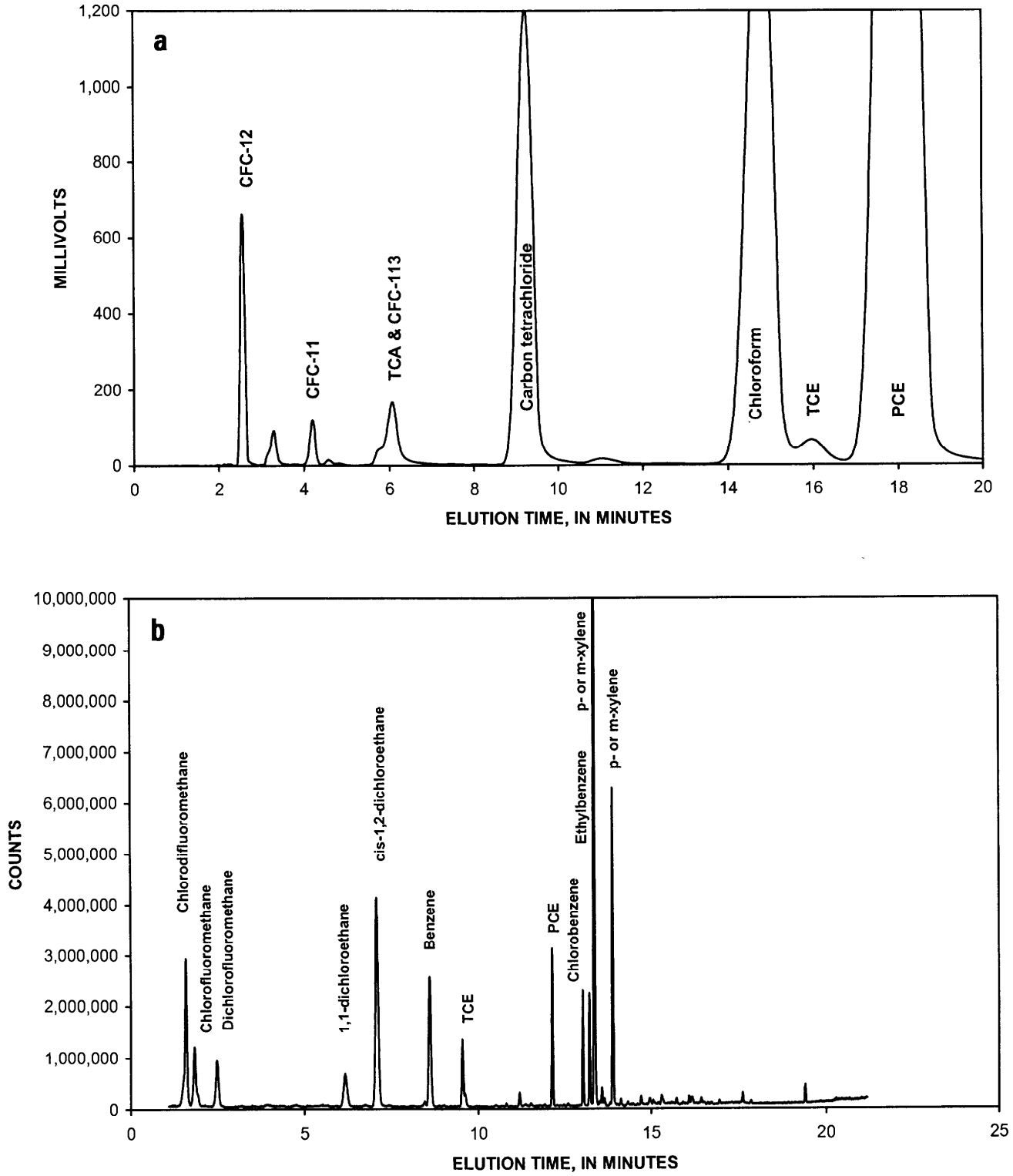


Figure 6. Example of (a) GC-ECD and (b) GC-MS analyses for a sample with numerous VOC peaks from a community-supply well in a fractured-rock aquifer in Virginia. Note scale of y-axis relative to scale of y-axis in figures four and five.

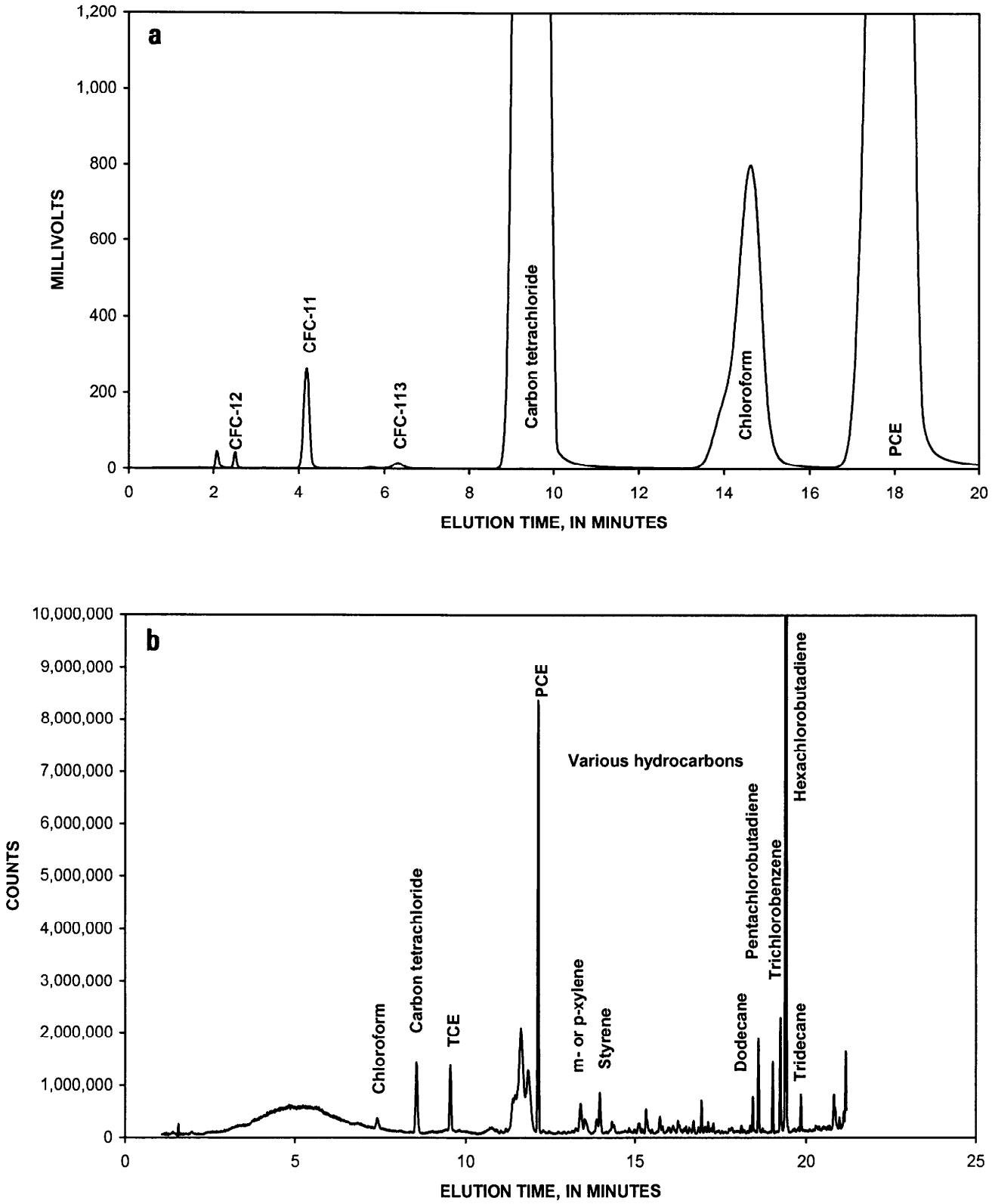


Figure 7. Example of (a) GC-ECD and (b) GC-MS analyses for a sample with numerous VOC peaks from a community-supply well in an unconsolidated Coastal Plain aquifer in Virginia. Note scale of y-axis relative to scale of y-axis in figures four and five.

CO-OCCURRENCE OF VOCs IN DRINKING WATER

Another issue of great importance with regard to VOCs in drinking water is that of co-occurrence of numerous VOCs, and the combined effect of the multiple VOCs even when individual concentrations are low. Thomas (1990) reports that VOCs should be treated as a class of substances due to the similarities of toxicity between individual VOCs and the similarities in target organs. Grady and Casey (2001) found that two or more VOCs occurred together in more than half of drinking water samples with VOC detections in the Northeast and Mid-Atlantic regions of the U.S., four or five compounds occurred together in 12% of the samples with VOC detections, and more than five compounds occurred together in 3% of samples with VOC detections. Squillace and others (1999) found that MTBE, PCE, TCE, and trichloromethane often occur together, likely because of widespread occurrence, not necessarily that they are used together. Westrick (1990) also found that the co-occurrence of numerous VOCs was common, but concluded that the co-occurrence was likely the result of common usage/disposal practices or from biotransformations of parent VOCs to common daughter products.

Utilizing non-CFC detections by both GC-ECD and GC-MS techniques, 12 compounds appeared in 30% or more of the samples (table 1). The NAWQA data are also included in table 1 in order to demonstrate that the co-occurrence of these compounds is being detected by all three methods for at least a few of the compounds (e.g. CCl_4, chloroform, PCE, and TCE). The 12 compounds that appeared in 30% or more of samples include 1,1,2,3,4,4-hexachloro-1,3-butadiene, 1,2,4-trichlorobenzene, 1,2,4-trimethylbenzene, 1,2-dichlorobenzene, 1,3,5-trimethylbenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, CCl_4, chloroform, and m-, p-, and/or o-xylene, PCE, and TCE. Many of the 85 samples analyzed by GC-MS have most, if not all, of the 12 compounds present (for example, sites 414 and 415). The results from the present investigation are consistent with those of Moran and others (2001), Rowe and others (2001), Squillace and others (1999), Westrick (1990), and Zogorski and others (2001) indicating that the predominant organic contaminants in ground water throughout the United States commonly co-occur and are compounds used as solvents, in gasoline, as refrigerants, and in organic synthesis.

SUMMARY AND CONCLUSIONS

An investigation to assess the occurrence of selected VOCs from sources of drinking water around the U.S. was conducted by the USGS Chlorofluorocarbon Laboratory using archived chromatograms and water samples originally from CFC analyses conducted between 1989 and 2000. Chromatograms from the CFC analyses were used to assess the occurrence of halogenated VOCs in water from 2,672 sites. The VOCs identified most frequently in this investigation using GC-ECD are the chlorinated solvents DCE, TCA, CCl_4, chloroform, TCE, and PCE. Seventy percent of the samples contained at least one VOC, and if the CFC data are included, 98% of the samples contained at least one VOC.

Archived water samples stored in flame-sealed borosilicate ampoules were analyzed using GC-MS to verify the identity of the frequently detected VOCs found on the CFC chromatograms as well as to identify non-halogenated VOCs that would not be detected by the GC-ECD. A total of 91 compounds were identified in the 85 samples analyzed by GC-MS. Twelve non-CFC compounds were identified in 30% or more of the samples analyzed by GC-ECD and GC-MS, including 1,1,2,3,4,4-hexachloro-1,3-butadiene, 1,2,4-trichlorobenzene, 1,2,4-trimethylbenzene, 1,2-dichlorobenzene, 1,3,5-trimethylbenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, CCl_4, chloroform, m-, p-, and/or o-xylene, PCE, and TCE. These twelve compounds routinely co-occur in water samples, however, this is likely the result of their pervasive use and continuous atmospheric presence, not necessarily that they are used in combination.

Results of the present investigation are consistent with those of numerous other state and national surveys in terms of the specific VOCs identified. A significant difference between this study and previous investigations, however, is the lower analytical detection limits (up to 5 orders of magnitude lower than the reporting level in previous investigations) achieved with the collection and analysis methods utilized by the USGS Chlorofluorocarbon Laboratory, and the fact that the data are internally consistent, unlike other national synthesis

Table 1. List of the 12 most commonly found compounds (other than CFCs) by GC-ECD and GC-MS from this investigation for the 85 sites analyzed by GC-MS

[Shaded rows indicate sites where NAWQA measurements were made (see text for details); GC-ECD, gas chromatograph-electron capture detector; GC-MS, gas chromatograph-mass spectrometer; NAWQA, National Water Quality Assessment Program; >, greater than; <, less than; ES, GC-ECD, peak area 100,000-499,999;EM, GC-ECD, peak area 500,000-999,999; EL, GC-ECD, peak area >1,000,000; *GC-ECD potential double peak, chloroform and trichloroethylene both likely present; GS, GC-MS, 90% certainty, peak area <10,000 counts; GM, GC-MS, 90% certainty, peak area 10,000-19,999 counts; GL, GC-MS, 90% certainty, peak area ≥ 20,000 counts; GES, GC-MS, tentative identification based on location, peak area <10,000 counts; GEM, GC-MS, tentative identification based on location, peak area 10,000-19,999 counts; GEL, GC-MS, tentative identification based on location, peak area ≥20,000 counts; NE, NAWQA data, concentration estimated because below minimum reporting level; N, NAWQA data, concentration above minimum reporting level; ---, not detected]

Counter from Appendix 1	1,1,2,3,4,4-Hexachloro-1,3-Butadiene	1,2,4-Trichloro-Benzene	1,2,4-Trimethyl-Benzene	1,2-Dichloro-Benzene	1,3,5-Trimethyl-Benzene	1,3-Dichloro-Benzene	1,4-Dichloro-Benzene	Carbon Tetrachloride	Chloroform	m, p, &/or o-Xylene	Tetrachloroethylene	Trichloroethylene
158	GL	---	---	---	---	GL	---	EL	EL,GL	GL	EL,GL	EL,GL
208	---	---	---	---	---	---	---	---	EL*,GL	---	EL,GL	EL*
219	GEL	---	---	---	---	---	---	ES	EL*,GL	---	EL,GL	EL*
406	GES	GES	GES	GES	---	---	---	ES	ES	---	---	---
407	GL	GM	GM	GL	GM	GL	GL	ES	EM	GES	EL	---
408	GES	GES	GES	---	---	---	---	---	---	---	---	---
409	GEM	GES	GES	GES	GES	GES	GES	GS,NE	EL*,GES,NE	---	EL,GES,NE	EL*,NE
410	GES	GES	---	GES	---	GES	GES	EM	ES,NE	---	EM	EM,GS
411	GES	GES	GES,NE	GES	---	GES	GES	EL	EL*,GES,NE	---	EM,GES	EL*,GL
412	GES	GES	GES,NE	GES	---	GES	GES	EL*,GS,NE	EL*,GES,NE	---	EL*,GES,NE	EL*,GL,N
414	GEL	GS	GS	GM	GS	GM	GM	ES	EM*	GS	EM	EM*
415	GEL	GES	GES	GEM	GES	GEM	GEM	EL	EL*,NE	GES	EM	EL*,GES,NE
416	GES	GES	GES	GES	GES	GES	GES	EL	EM*	GES	EL	EM*
417	---	GES	GES	GES	---	GES	GES	EL	ES*	---	ES	ES*
418	GES	GES	GES,N	GES	---	GES	GES	EL	EL	---	EL	EL
419	GES	GES	GES	GES	---	GES	GES	ES	ES*	---	EM	ES*
420	---	GES	GES	GES	---	GES	GES	---	ES*	---	ES	ES*
421	GES	GES	GES	GES	---	GES	GES	---	ES*	GES	ES	ES*,GES
422	GES	GES	GES	GES	---	GES	GES	EL	EL*,GES,NE	---	EL*,GES,NE	EL*,GES,NE
423	GEL	GES	GES	GES	GES	GES	GES	ES	EM,NE	GES	EM	---
424	GES	GES	GES	GES	GES	GES	GES	EL,GES	EL*,GES	GES	EL	EL*,GM
425	GEL	GES	GES	GES	GES	GES	GES	ES	EL*,GES,NE	---	EM	EL*,GES
427	GES	GES	GES	GES	---	GES	GES	ES	---	---	---	---
428	---	GES	GES	GES	---	GES	GES	EL	EL*,NE	---	EL	EL*
429	GEM	GL	---	---	GS	GS	GS	EL	EL*	---	ES	EL*
430	GL	GS	GS	---	GS	GS	GS	EL*,GL,N	EL*,GS,N	---	EL,GL,N	EL*,GM,N
432	GL	GS	GS	GL	GM	GL	GL	---	---	GS	ES	---
433	GL	GS	GS	GL	GM	GM	GL	EL	EL*	GS	EL	EL*,GL,N
434	GL	GS	GS	GM	GS	GM	GM	EL	EL*	GES	EL	EL*,GES
436	GEL	GES	GES	GEM	GES	GEM	GEM	ES	ES*	GES	ES	---
437	GEM	GES	GES	GES	GES	GES	GES	---	ES	GES	ES	---
438	GS	GS	GS	GS	GS	GS	GS	---	---	GS	ES	---
950	---	---	---	---	---	---	---	ES	ES*	---	EL	---
951	---	GES	---	---	---	---	---	EL	---	---	---	---
952	GM	GM	---	---	---	---	---	EL	ES*	---	EM	---
954	---	---	---	---	---	---	---	---	---	---	---	---
956	GES	GS	GES	GES	GES	GES	GES	ES	---	---	EL,GES	---
957	GL	GL	GES	GES	---	GES	GES	---	---	GES	ES	---
958	---	GM	GES	---	---	---	---	EM	ES	---	---	---
959	---	GS	---	---	---	---	---	ES	---	---	ES	---
961	---	---	---	---	---	---	---	EL	ES	---	ES	---
967	GM	GM	GS,N	---	---	---	---	EM	ES*,NE	NE	EL	ES*
968	GES	GES	GES	GES	---	GES	GES	---	ES*	---	---	ES*
969	GES	GES	GES	GES	GES	GES	GES	---	EM*	---	ES	EM*
972	GL	GM	GM	GES	GES	GES	GS	ES	---	---	ES	---
973	GES	GEM	GES	GES	GES	GES	GES	ES	ES*	---	ES	ES*

Table 1. List of the 12 most commonly found compounds (other than CFCs) by GC-ECD and GC-MS from this investigation for the 85 sites analyzed by GC-MS--Continued

Counter from Appendix 1	1,1,2,3,4,4-Hexachloro-1,3-Butadiene	1,2,4-Trichloro-Benzene	1,2,4-Trimethyl-Benzene	1,2-Dichloro-Benzene	1,3,5-Trimethyl-Benzene	1,3-Dichloro-Benzene	1,4-Dichloro-Benzene	Carbon Tetrachloride	Chloroform	m, p, &/or o-Xylene	Tetrachloroethylene	Trichloroethylene
974	GM	GS	GS	GES	GES	GES	GES	EM	EL*,NE	---	EL	EL*
976	GES	GES	---	---	---	GES	GES	EL	EM*,GES	---	EL	EM*
977	GES	GES	---	GES	---	GES	GES	ES,GES	---	---	ES	---
980	GS	GS	GES	GS	GES	GS	GS	ES,GES	---	---	ES	---
981	GES	GES	GES	GES	---	GES	GES	---	ES*	---	---	ES*
983	GES	GES	GES	GES	---	GES	GES	ES	ES*	---	---	ES*
985	GM	GS	GES	GES	GES	GES	GES	EM	---	---	---	---
986	GEM	GEM	GES	GES	GES	GES	GES	EL	EL*	---	---	EL*
987	GES	GS	GES	GES	GES	GES	GES	ES	---	---	ES	---
988	GES	GEM	---	---	---	---	---	---	---	---	---	---
989	GES	GES	GES	---	---	---	---	ES	ES*	---	ES	ES*
990	---	GES	GES	---	---	---	---	EM	ES*	---	EL	ES*
991	GES	GES	GES	GES	GES	GES	GES	---	ES*	---	---	ES*
992	GES	GES	GES	GES	---	GES	GES	---	ES*	---	ES	ES*
994	GES	GES	GES	GES	---	---	---	ES	EL*,GES	---	EL,GES	EL*
995	GES	GS	GES	---	---	GES	---	EL	EL,GES,N	---	EL,GES,NE	EL
996	---	GES	---	---	---	---	---	ES	---	---	---	---
999	GL	---	---	NE	GL	---	NE	EL	EL*,GL,N	GL	EL,GL,N	EL*,GL
1000	GL	---	---	GL,NE	---	NE	N	EL	EL*,GL,N	GL	EL,GL,NE	EL*,GL,N
1006	---	---	---	GL	GL	---	GL	EL	EM,GL,N	GL	EL,GL,N	EL,GL
1012	---	---	---	GL	---	---	GL	EL	EL,GL,N	GL	EL,GL,NE	EL,GL
1022	---	---	---	---	---	---	NE	EM	EL*,GL,N	GL	EL,GL,N	EL*,GL,NE
1024	GL	---	---	---	---	GEL	GEL	EL	EL*,GL	GL	EL,GL	EL*,GL
1645	GL	---	---	---	---	GL	NE	EL	EL*,GL,N	GL	EL,GL,N	EL*,GL,NE
1839	GL	GM	GL	GM	GS	GM	GM	---	GES	GL	GES	GES
1909	GL	GL	---	GEL	---	---	---	EL,GL	EL*,GEL	GL	EL,GL	EL*,GL
1958	GL	---	---	---	---	---	---	---	---	---	GES	GL
1960	GL	---	---	---	---	---	---	---	---	---	GL	GL
1976	GL	---	---	---	---	---	---	---	---	---	---	GL
1992	GEL	---	---	---	---	---	---	EL	EL	GL	EL,GL	EL,GL
2040	---	---	---	---	---	---	---	ES	ES*	---	EM	ES*
2061	---	---	---	---	---	---	---	EM	EL*	GL	EL,GL	EL*,GL
2113	---	---	---	---	---	---	---	ES	EL*	---	EL	EL*
2116	GL	---	---	---	---	---	---	EL	EM*	---	EM	EM*,GL
2254	---	---	---	GL	---	GES	---	ES	EL*,GM	---	EL	EL*
2255	GEM	GES	GL	GES	GM	GES	GES	EL	EL,GL	GS	EL,GS	EL,GES
2256	GL	GS	GL	GS	GS	GS	GS	ES	EL,GES	GM	EL,GL	EL
2257	GS	GS	GL	GES	GS	---	GES	ES	EL*,GM	GES	EL,GES	EL*
2258	GEL	GES	GL	GES	GES	GES	GES	ES	EL*,GM	GEL	EL,GL	EL*,GS

investigations that utilized data from numerous sources that had different collection and analysis procedures. While concentrations for VOCs other than CFC-11, CFC-12, and CFC-113 are not quantified in this investigation, the detections provide evidence for aquifer susceptibility to anthropogenic contamination, and early warning of potential contamination problems. Previous non-detects by other methods that do not have the same low detection limits have been used to support claims of safety in water supplies; however, the detections of various VOCs at the parts per quadrillion level using the GC-ECD should be viewed as evidence of anthropogenic influence on water supplies.

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